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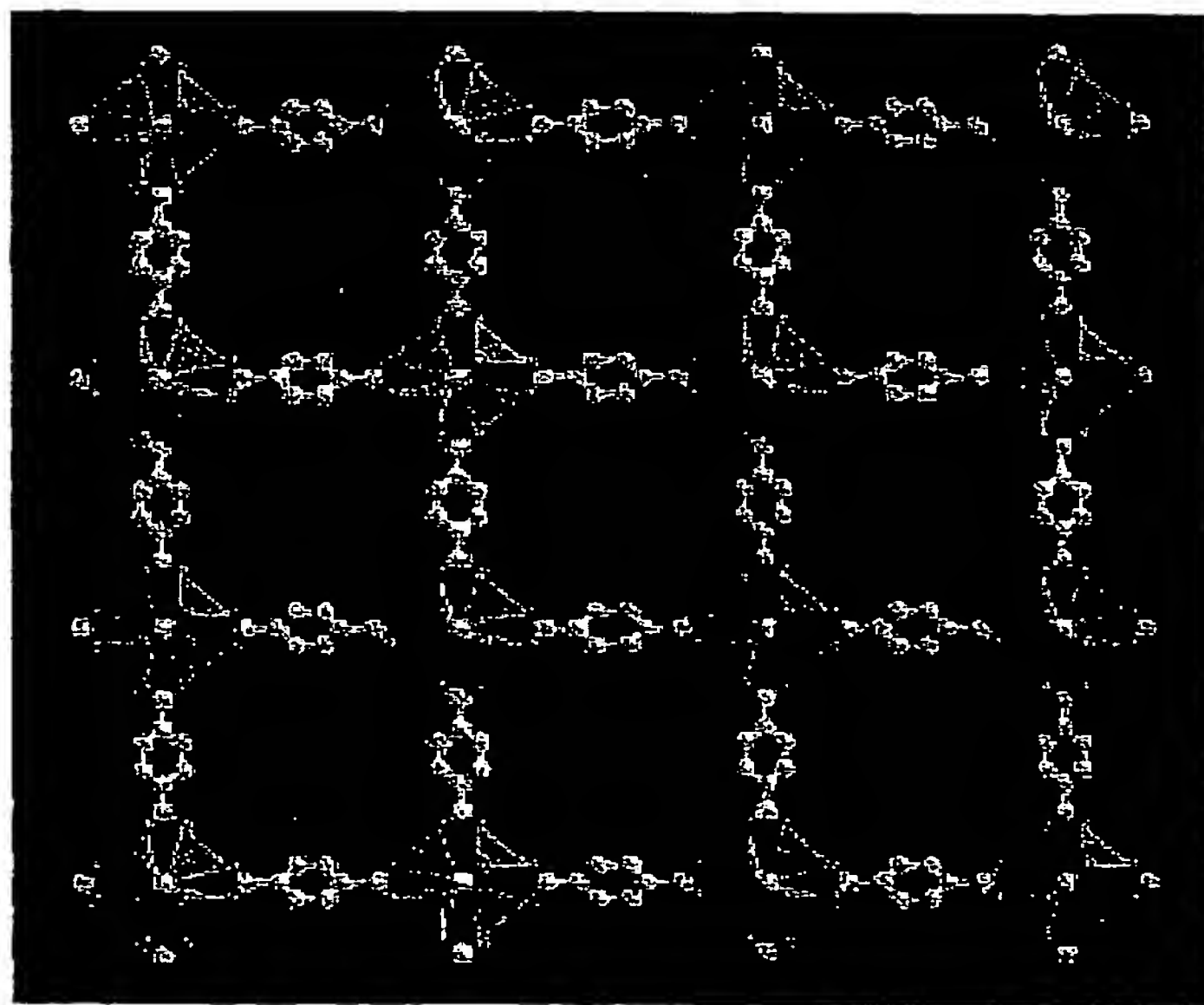
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[Continued on next page]

(54) Title: ISORETICULAR METAL-ORGANIC FRAMEWORKS, PROCESS FOR FORMING THE SAME, AND SYSTEMATIC DESIGN OF PORE SIZE AND FUNCTIONALITY THEREIN, WITH APPLICATION FOR GAS STORAGE



(57) Abstract: The ability to design and construct solid-state materials with pre-determined structures is a grand challenge in chemistry. An inventive strategy based on reticulating metal ions and organic carboxylate links into extended networks has been advanced to a point that allows the design of porous structures in which pore size and functionality can be varied systematically. MOF-5, a prototype of a new class of porous materials and one that is constructed from octahedral Zn-O-C clusters and benzene links, was used to demonstrate that its 3-D porous system can be functionalized with the organic groups, -Br, -NH<sub>2</sub>, -OC<sub>3</sub>H<sub>7</sub>, -OC<sub>5</sub>H<sub>11</sub>, -H<sub>4</sub>C<sub>2</sub> and -H<sub>4</sub>C<sub>4</sub>, and its pore size expanded with the long molecular struts biphenyl, tetrahydropyrene, pyrene, and terphenyl. The ability to direct the formation of the octahedral clusters in the presence of a desired carboxylate link is an essential feature of this strategy, which resulted in the design of an *isoreticular* (having the same framework topology) series of sixteen well-defined materials whose crystals have open space representing up to 91.1% of the crystal volume, and homogeneous periodic pores that can be incrementally varied from 3.8 to 28.8 angstroms. Unlike the unpredictable

nature of zeolite and other molecular sieve syntheses, the deliberate control exercised at the molecular level in the design of these crystals is expected to have tremendous implications on materials properties and future technologies. Indeed, data indicate that members of this series represent the first monocrystalline mesoporous organic/inorganic frameworks, and exhibit the highest capacity for methane storage (155 cm<sup>3</sup>/cm<sup>3</sup> at 36 atm) and the lowest densities (0.41 to 0.21 g/cm<sup>3</sup>) attained to date for any crystalline material at room temperature.

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ISORETICULAR METAL-ORGANIC FRAMEWORKS, PROCESS FOR  
FORMING THE SAME, AND SYSTEMATIC DESIGN OF PORE SIZE AND  
FUNCTIONALITY THEREIN, WITH APPLICATION FOR GAS STORAGE

5                   **CROSS-REFERENCE TO RELATED APPLICATIONS**

          This application claims the benefit of U.S. Provisional Applications  
S.N. 60/287,489, filed April 30, 2001; and S.N. 60/340,623, filed December 14,  
2001.

10                   **STATEMENT REGARDING FEDERALLY SPONSORED  
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15           invention.

**BACKGROUND OF THE INVENTION**

          The present invention relates generally to metal-organic frameworks,  
and more specifically to such frameworks, which are reticulated into a predetermined  
porous material with a tailored pore size and/or functionality, and their application as  
20           sorbents for storing gases such as methane.

          One of the great challenges in porous materials is the design and the  
achievement of a desired porous material with a tailored pore size and/or  
functionality. To date, it has not been possible to consistently and efficiently (with a  
high yield) render porous materials having predetermined characteristics.

25           A particular goal is to alter chemical composition, functionality, and  
molecular dimensions without changing the underlying topology. See A. Stein, S.  
W. Keller and T. E. Mallouk, *Science* **259**, 1558 (1993); and P. J. Fagan and M. D.  
Ward, *Sci. Am.* **267**, 48 (1992). Although this has been a dream of scientists and  
engineers for most of the last century, little progress has been achieved largely due to  
30           lack of control over the course of molecular assembly and the inability to predict the  
orientation of atomic groups in crystals. Unlike the process of building organic  
molecules, where it is possible to execute the total synthesis of complex ring systems  
in a step-by-step fashion, the insolubility of extended solids generally necessitates

that their assembly be accomplished in a single step. See O.M. Yaghi, M. O'Keeffe, and M. Kanatzidis, *J. Solid State Chem.* **152**, 1 (2000).

Porous materials are mainly used for gas/liquid separation, catalysis, luminescence-based sensors, and gas storage. To achieve a specific application, a porous material with a defined pore size and function is needed. To achieve these challenging objectives, many scientists have devoted their knowledge and programs to develop this area.

A stable, porous metal-organic framework was disclosed recently. See Li, Hailian, Mohamed Eddaoudi, M. O'Keeffe and O.M. Yaghi, "Design and synthesis of an exceptionally stable and highly porous metal-organic framework," *Nature*, Vol. 402, pp. 276-279 (18 November 1999). This framework was formed by diffusing triethylamine into a solution of zinc (II) nitrate and H<sub>2</sub>BDC (benzenedicarboxylic acid) in N,N'-dimethyl-formamide/chlorobenzene. This resulted in the deprotonation of H<sub>2</sub>BDC and its reaction with Zn<sup>2+</sup> ions. The rendered cubic crystals were designated metal-organic framework (MOF)-5 and were found to comprise an extended, porous network having a three-dimensional intersecting channel system with 12.94 Å spacing between centers of adjacent clusters.

The diffusion of base into the solution is generally accepted in the literature as being an important step in the process of fabricating such MOFs. See, for example, Eddaoudi, Mohamed et al., "Modular Chemistry: Secondary Building Units as a Basis for the Design of Highly Porous and Robust Metal-Organic Carboxylate Frameworks," *Accounts of Chemical Research*, Vol. 34, No. 4, pp. 319-330 (Web publication date 17 February 2001). This article states that a key step to obtaining crystals is to slowly diffuse an organic amine into the reaction mixture.

Although the MOF-5 crystalline structure described in *Nature*, *supra*, has desirable characteristics, the process for making the structure actually renders a mixture of crystalline structures, the MOF-5 being a relatively low percentage of the mix. Further, the *Nature* MOF-5 structure appears to be limited to a single benzene ring as a linkage between adjacent Zn<sub>4</sub>(O)O<sub>12</sub>C<sub>6</sub> clusters.

Others have recently pursued the assembly of extended structures from molecular building blocks. See V.A. Russell, C.C. Evans, W.J. Li and M.D. Ward, *Science* **276**, 575 (1997); Y.H. Kiang, G.B. Gardner, S. Lee, Z.T. Xu and E.B. Lobkovsky, *J. Am. Chem. Soc.* **121**, 8204 (1999); and B.F. Hoskins and R. Robson, *J. Am. Chem. Soc.* **111**, 5962 (1989).

Researchers have attempted to formulate frameworks having longer links between adjacent clusters. Synthesis of open frameworks by assembly of metal ions with di-, tri- and poly-topic N-bound organic linkers such as 4,4'-bipyridine has produced many cationic framework structures. However, attempts to evacuate/exchange guests within the pores usually unfortunately results in the collapse of the host framework.

Further, expanded structures have been formed using long links to increase the spacing between vertices in a net, yielding void space proportional to the length of the linker. However, although such expanded structures provide for large pores (and one would therefore expect a high porosity), in practice they are often found to be highly undesirably interpenetrated and to have low porosity.

Thus, it would be desirable to provide a reproducible metal-organic porous material advantageously having a predetermined pore size and function. It would further be desirable to provide such a porous material which desirably retains its topology even with varied linkage compounds. Yet further, it would be desirable to provide a high yielding method for preparing such porous materials. Still further, it would be desirable to provide such a porous material which may advantageously store gases at desirable pressures such as the predominant natural gas methane.

### SUMMARY OF THE INVENTION

The present invention addresses and solves the above-mentioned problems by providing an isoreticular metal-organic framework (IRMOF), consisting essentially of a plurality of secondary building units (SBUs), each of the plurality of SBUs comprising an  $M_4O(CO_2)_6$  cluster; and a compound linking adjacent SBUs, the linking compound comprising a linear ditopic carboxylate having at least one phenyl group and at least one functional group X attached to the at least one phenyl group.



The inventive IRMOF has a substantially permanent porosity and is stable, with or without the presence of guest molecules.

A method of forming the inventive isorecticular metal-organic framework (IRMOF) comprises the step of dissolving at least one metal salt and at least one linear ditopic carboxylate in a solvent to form a solution. The solution is then crystallized to form the IRMOF. The crystallizing step is carried out by at least one of: leaving the solution at room temperature; adding a diluted base to the solution to initiate the crystallization; diffusing a diluted base into the solution to initiate the crystallization; and transferring the solution to a closed vessel and heating to a predetermined temperature.

The selected conditions are ideal to form the cluster  $M_4O(CO_2)_6$  (the SBU). The SBUs in the case of IRMOFs occupy the corners of the cube, and ditopic linkers link them.

Further, member(s) of the IRMOFs series have been found to have very high methane storage capacity. Specifically, the inventive IRMOF(s) have been found to have a methane storage capacity of about 155 cm<sup>3</sup>/cm<sup>3</sup>, which is the highest methane storage capacity in any crystalline porous material to date.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

Objects, features and advantages of the present invention will become apparent by reference to the following detailed description and drawings, in which:

Figure 1 is a diagrammatic representation of IRMOF 1 of the present invention;

Figure 2a is a graphic representation of an XRPD of IRMOF-1 for Method 1 of the present invention;

Figure 2b is graphic representation of an XRPD of IRMOF-1 for Method 2 of the present invention;

Figure 2c is a graphic representation of an XRPD of IRMOF-1 for Method 3 of the present invention;

Figure 3 is a diagrammatic representation of a crystal structure for IRMOF-3 of the present invention;

Figure 4a is a graphic representation of an XRPD of IRMOF-3 of the

present invention;

Figure 4b is a graphic representation of a simulated XRPD of IRMOF-3;

Figure 5 is a graphic representation of an InfraRed spectrum for IRMOF-3 of the present invention;

Figure 6 is a graphic representation of TGA on  $\text{Zn}_4\text{O}(\text{BDC}[\text{NH}_2])_3 \cdot (\text{DEF})_x$  of the present invention;

Figure 7 is a graphic representation of an InfraRed spectrum for  $\text{Zn}_4\text{O}(\text{BDC}[\text{NH}_2])_3 \cdot (\text{CHCl}_3)_x$  of the present invention;

Figure 8 is a graphic representation of TGA  $\text{Zn}_4\text{O}(\text{BDC}[\text{NH}_2])_3 \cdot (\text{CHCl}_3)_x$  of the present invention;

Figure 9 is a graphic representation of an  $\text{N}_2$  Sorption on IRMOF-3 @ 77K of the present invention;

Figure 10 is a graphic representation of an organic vapor sorption at RT on IRMOF-3 of the present invention;

Figure 11 is a diagrammatic representation of a crystal structure for IRMOF-6 of the present invention;

Figure 12a is a graphic representation of an XRPD of IRMOF-6 of the present invention;

Figure 12b is a graphic representation of a simulated XRPD of IRMOF-6 of the present invention;

Figure 13 is a graphic representation of an InfraRed spectrum for IRMOF-6;

Figure 14 is a graphic representation of a TGA for IRMOF-6,  $\text{Zn}_4\text{O}(\text{BDC}[\text{C}_2\text{H}_4])_3 \cdot (\text{DEF})_x$  of the present invention;

Figure 15 is a graphic representation of an InfraRed spectrum for  $\text{Zn}_4\text{O}(\text{BDC}[\text{C}_2\text{H}_4])_3 \cdot (\text{CHCl}_3)_x$ ;

Figure 16 is a graphic representation of a TGA on  $\text{Zn}_4\text{O}(\text{BDC}[\text{C}_2\text{H}_4])_3 \cdot (\text{CHCl}_3)_x$  of the present invention;

Figure 17 is a graphic representation of sorption on  $\text{Zn}_4\text{O}([\text{H}_4\text{C}_2]\text{BDC})_3$  of the present invention;

Figure 18 is a diagrammatic representation of a crystal structure for IRMOF-7;

Figure 19a is a graphic representation of XRPD of IRMOF-7;

Figure 19b is a graphic representation of a simulated XRPD of IRMOF-7 of the present invention;

Figure 20 is a graphic representation of XRPD of IRMOF-8 of the present invention;

Figure 21 is a diagrammatic representation of a crystal structure for IRMOF-9 of the present invention;

Figure 22a is a graphic representation of XRPD of IRMOF-9 of the present invention;

Figure 22b is a graphic representation of simulated XRPD of IRMOF-9;

Figure 23 is a graphic representation of an InfraRed spectrum for IRMOF-9 of the present invention;

Figure 24 is a diagrammatic representation of a crystal structure for IRMOF-12 of the present invention;

Figure 25a is a graphic representation of XRPD of IRMOF-12 of the present invention;

Figure 25b is a graphic representation of simulated XRPD of IRMOF-12 of the present invention;

Figure 26 is a graphic representation of InfraRed spectrum for IRMOF-12 of the present invention;

Figure 27 is a diagrammatic representation of a crystal structure for IRMOF-11 of the present invention;

Figure 28a is a graphic representation of XRPD of IRMOF-11 of the present invention;

Figure 28b is a graphic representation of a simulated XRPD of IRMOF-11 of the present invention;

Figure 29 is a graphic representation of an InfraRed spectrum for IRMOF-11 of the present invention;

Figure 30 is a diagrammatic representation of a crystal structure for



IRMOF-14 of the present invention;

Figure 31a is a graphic representation of XRPD of IRMOF-14 of the present invention;

Figure 31b is a graphic representation of a simulated XRPD of IRMOF-14 of the present invention;

Figure 32 is a graphic representation of an InfraRed spectrum for IRMOF-14 of the present invention;

Figure 33 is a graphic representation of XRPD of IRMOF-13 of the present invention;

Figure 34 is graphic representation of an InfraRed spectrum for IRMOF-13 of the present invention;

Figure 35 is a graphic representation of XRPD of IRMOF-15 of the present invention;

Figure 36 is a graphic representation of an InfraRed spectrum for IRMOF-15 of the present invention;

Figures 37 - 52 are single crystal X-ray structures of IRMOF-1 to -16, respectively. Color scheme and drawings conditions: Zn (blue polyhedra), O (red spheres), C (black and gray spheres), Br (green spheres), amino-groups in Fig. 3 (blue spheres). All hydrogen atoms and guests are omitted, and only one orientation of disordered atoms, common to most of the links and in some Zn-O-C units, is shown for clarity;

Figs. 53A - 53L depict various ligands;

Fig. 54 (Bottom to top): For IRMOF-1-16, A) the calculated (using cerius<sup>2</sup> version 4.2) percent free volume (yellow), B) crystal densities (light brown), and C) free diameter (green) and fixed diameter (blue), respectively obtained by measuring the diameter of a sphere that would pass through the aperture and another that would fit inside the pores without overlapping with framework atoms; and

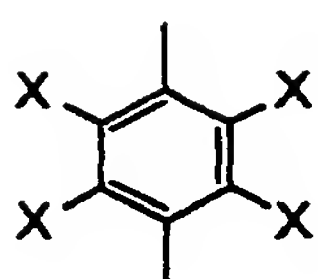
Fig. 55 (A) Thermogravimetrogram for IRMOF-6 including its (B) gas and organic vapor isotherms, and (C) its voluminous uptake of methane gas. The stability of two of the most open IRMOFs (12 and 14) is shown by their (D) X-ray powder diffraction patterns before and after evacuation of guests trapped in the pores.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

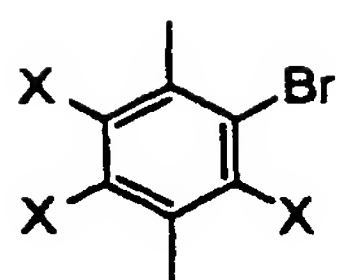
The present invention is predicated upon the unexpected and fortuitous discovery that an extremely stable (with or without the presence of guest molecules within the pores of the framework) and highly (substantially permanently) porous isorecticular metal-organic framework having a topology similar to that shown in Figure 1 may be formed, even when utilizing linkers other than benzenedicarboxylate. The links in Figure 1 are single, unsubstituted benzene rings. Contrary to the established literature, it has been fortuitously found that the benzene ring of the dicarboxylate may be substituted with a functional group and/or the link may comprise a plurality of benzene rings (forming a horizontal line, a vertical line, or both, ie. the plurality of rings may be as tall as desired and/or as fat as desired), while retaining a stable network with very high porosity and substantially no undesirable interpenetration.

This fortuitous discovery allows for the fabrication of desired porous materials with predetermined, tailored pore sizes and/or functionalities, depending upon the ligand(s) used.

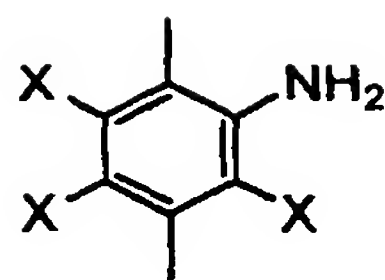
Some exemplary linking compounds/ligands are depicted immediately below (note that the numbers appearing below the compounds correspond to the number of the IRMOF of which they are part), where X stands for a functional group, such as, for example, hydrogen, amines, halides. X can also be an R group, for example, linear, substituted or cyclo alkanes ( $\text{CH}_3\text{-(CH}_2\text{)}_n\text{-CH}_2\text{-}$ )  $n=0, 1, 2\ldots$ , alkenes (double bond), alkynes (triple bond), chains, or ether O-R, where R is the same as mentioned before. More specifically, X may comprise amines (primary, secondary, tertiary); aromatic amines, pyridine, and pyrimidine like 5 or 6 membered rings; halides including substituted -RX; alcohols: ROH; thiols: RSH; sulfonates -R-SO<sub>3</sub>; nitro groups -R(NO<sub>2</sub>); phosphates -R-PO<sub>2</sub><sup>-</sup>; epoxides; alkanes CH<sub>2</sub>(CH<sub>3</sub>)<sub>n</sub>CH<sub>2</sub>  $n=0, 1 \ldots$ ; alkenes; alkynes; aldehydes (RCOH); ketones (-RCOR); esters RCO<sub>2</sub>R; carboxylic acids; cycloalkanes; cycloalkenes; cycloalkynes; silyls derivatives; boranes derivatives; and ferrocenes and other metallocenes.



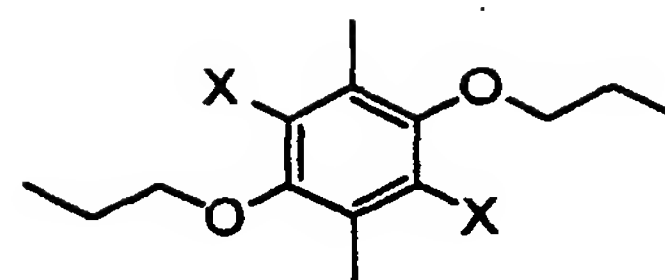
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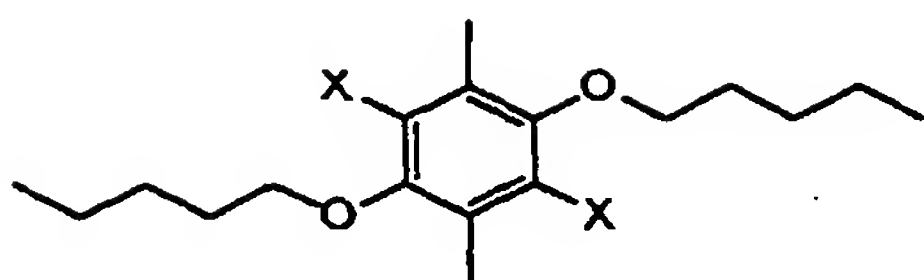
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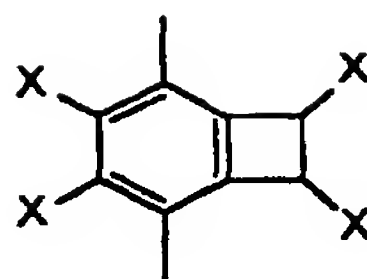
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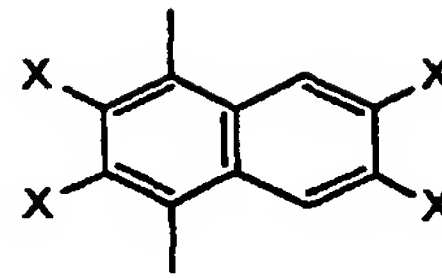
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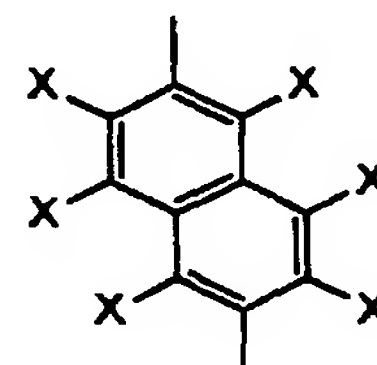
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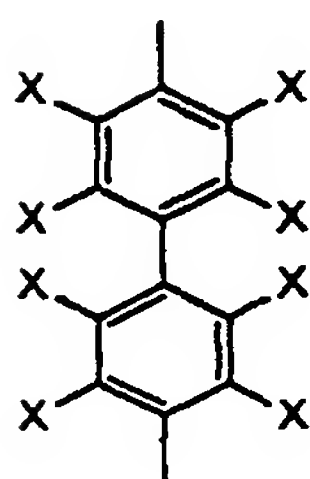
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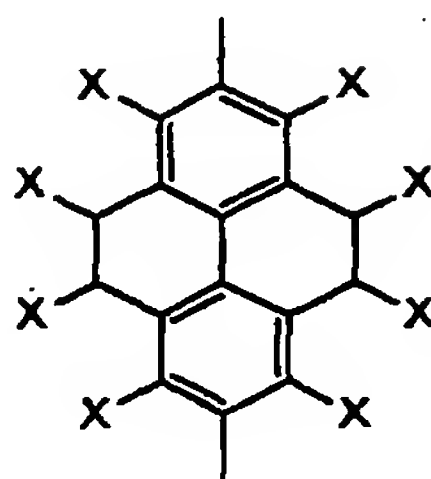
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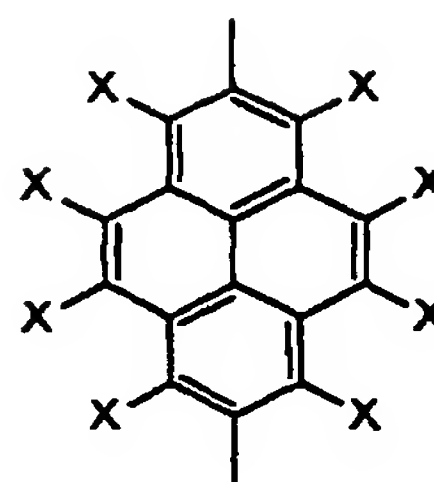
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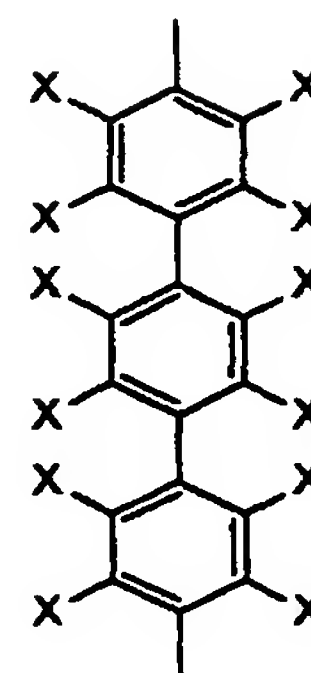
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The present invention discloses the first series of tailored porous materials. *Iso*-reticular Metal-Organic Frameworks (IRMOFs) are important avenues toward consistently and efficiently (with a high yield) rendering stable, substantially permanently porous materials having a predetermined characterization. "Reticular" is an adjective defined in Random House Webster Unabridged Dictionary as "having the form of a net; netlike." Isoreticular can thus be defined as: having the same network topology.

In general, MOFs are formed by a combination of metal cations and polydentate organic linkers. The incorporation of organic linkers as an integral part into the framework is of great advantage due to the ability to apply all the well-established organic chemistry knowledge to functionalize the linker. The present invention shows that it is possible to design porous materials, "IRMOFs," with tailored pores sizes and functionality/ies, an unprecedented achievement to date.

In order to design a target extended structure with the same precision practiced in organic synthesis, it is desirable that (a) the starting building blocks have the relevant attributes necessary to assemble into the skeleton of the desired structure, (b) the synthesis be adaptable to using derivatives of those building blocks to produce structures with the same skeleton but different functionalities and dimensions, and importantly, (c) the products should be highly crystalline to allow the full characterization of their atomic connectivity by X-ray diffraction techniques.

The most notable example of a truly porous metal-organic frameworks (MOF) is MOF-5 in which octahedral Zn-O-C clusters are linked by benzene struts to reticulate into a primitive cubic structure (Fig. 1). The exceptional rigidity and high porosity of MOF-5 led to its use as a target in studies aimed at overcoming the three challenges outlined immediately hereinabove and also to developing the next phase of this chemistry, namely, functionalization of the pores and systematic variation of their size--aspects that are highly sought after in solid-state chemistry and only recently pursued in crystalline zeolite research. See C.W. Jones, K. Tsuji and M.E. Davis, *Nature* **393**, 52 (1998).

In the present invention, we disclose the successful, systematic design and construction of a series of frameworks having structures based on the skeleton of

MOF-5, wherein the pore functionality and size have been varied without changing the original cubic topology. Furthermore, the implications and scope of such controlled design are revealed by the properties of several members of this series, where pore sizes in the mesoporous range ( $>20 \text{ \AA}$ ) have been achieved, the highest methane storage capacity measured, and the lowest crystal density of any material has been attained.

In general, a specific metal salt and a linear ditopic carboxylate were dissolved in a predefined solvent. Depending on the solubility and the acidity of the ligand, the mixture can either be left at room temperature to crystallize, and/or if necessary or desired, a diluted base is added or allowed to diffuse into the mixture to initiate the reaction, and/or transferred to a closed vessel and heated to a predetermined, precise temperature.

The selected conditions are ideal to form the cluster  $M_4O(CO_2)_6$  (also called a secondary building unit (SBU)). The SBU in the case of IRMOFs occupy the corners of the cube, and ditopic linkers link them. The resultant dimension, pore size and free volume are related to linkers: Expanded structure results from expanding the linker to a series of linear benzene rings, and reducing the pore volume is generated by introducing functional groups on the benzene rings (those pointing toward the inner cavities).

Some crystalline metal-organic microporous materials are broadly disclosed in U.S. Patent No. 5,648,508, which is incorporated herein by reference in its entirety.

An isorecticular metal-organic framework (IRMOF) according to the present invention consists essentially of a plurality of secondary building units (SBUs), each of the plurality of SBUs comprising an  $M_4O(CO_2)_6$  cluster. A compound links adjacent SBUs, the linking compound comprising a linear ditopic carboxylate having at least one phenyl group and at least one functional group X attached to at least one phenyl group. The IRMOF formed has a substantially permanent porosity and is very stable, with or without the presence of guest molecules.

M in the SBU is a metal cation of a metal selected from the group consisting of beryllium, zinc, cadmium, mercury, and any of the transition metals (in the periodic table, scandium through copper, yttrium through silver, lanthanum through



gold, and all known elements from actinium on). X may be any suitable functional group as necessary and/or desired. In the preferred embodiment, X is selected from the group enumerated hereinabove.

A method of forming an isorecticular metal-organic framework (IRMOF) comprises the step of dissolving at least one metal salt and at least one linear ditopic carboxylate in a solvent to form a solution. The solvent may be any suitable solvent, however, in the preferred embodiment, the solvent is any nitrogen containing solvent having a boiling point of less than about 250°C. The solution is then crystallized to form the targeted IRMOF.

The metal salt is formed from a metal cation and an anion, the metal cation being a cation of a metal selected from the group consisting of beryllium, zinc, cadmium, mercury, and any of the transition metals. The anion is selected from the group consisting of F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, ClO<sup>-</sup>, ClO<sub>2</sub><sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, OH<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, CO<sub>3</sub><sup>2-</sup>, and PF<sub>6</sub><sup>-</sup> and organic counter ions such as acetate CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>, triphlates CF<sub>3</sub> SO<sub>3</sub><sup>-</sup>.

In the preferred embodiment, the linear ditopic carboxylate/carboxylic acid has at least one phenyl group. In a further preferred embodiment, at least one functional group X is attached to the at least one phenyl group. X is as defined hereinabove.

The crystallizing step is carried out by: leaving the solution at room temperature; adding a diluted base to the solution to initiate the crystallization; diffusing a diluted base into the solution to initiate the crystallization; and/or transferring the solution to a closed vessel and heating to a predetermined temperature.

It has been unexpectedly and fortuitously discovered in the present invention that, whereas diffusion of base into the solution has been recognized as a key step in the formation of MOFs, the method of the present invention has advantageously formed very high yields (about 93%) of pure IRMOF either without any base at all, or by addition (not diffusion) of base into the solution.

It is to be understood that the linking compounds/ligands possessing multi- and/or poly-dentate functional groups may or may not bring with them one or more corresponding counter cations, such as, for example, H<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>,

$\text{Sr}^{2+}$ , ammonium ion, alkylsubstituted ammonium ions, and arylsubstituted ammonium ions, or one or more counter anions, such as, for example,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}^-$ ,  $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{OH}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{PF}_6^-$  and organic counter ions such as acetate  $\text{CH}_3\text{CO}_2^-$ , triphlates  $\text{CF}_3\text{SO}_3^-$ .

5           The crystalline microporous materials of the present invention may be synthesized using metal ions having distinctly different coordination geometries, in combination with a ligand possessing multi- and/or poly-dentate functional groups.

10           It is to be understood that the metal ions may be in the form of a metal salt formed from the metal ions with anions, such as, for example,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}^-$ ,  $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{OH}^-$ ,  $\text{HCO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{B}_4\text{O}_7^{2-}$  and  $\text{PF}_6^-$  and organic counter ions such as acetate  $\text{CH}_3\text{CO}_2^-$ , triphlates  $\text{CF}_3\text{SO}_3^-$ .

          Note that in various crystal structure figures, the yellow spheres represent the largest van der Waals spheres that would fit in the cavities without touching the frameworks.

15           The design of an isorecticular metal-organic framework (IRMOF) series based on MOF-5 was initiated by determining the reaction conditions necessary to produce, in situ, the octahedral cluster with a ditopic linear carboxylate link. In this context, the original low yielding synthesis of MOF-5 (described in Nature 402, *supra*) was re-examined and developed into a high yielding preparation: an  
20    $\text{N,N}'$ -diethylformamide (DEF) solution mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and the acid form of 1,4-benzenedicarboxylate (BDC) are heated ( $85\text{--}105^\circ\text{C}$ ) in a closed vessel to give crystalline MOF-5,  $\text{Zn}_4\text{O}(\text{R}_1\text{-BDC})_3$  ( $\text{R}_1 = \text{H}$ ), hereafter termed IRMOF-1, in 90% yield. The simplicity of the method and the facility with which IRMOF-1 can be obtained were some of the indications that the use of other ditopic carboxylate links under closely  
25   related, if not identical, conditions would yield the same type of frameworks having diverse pore sizes and functionalities.

          Indeed, employing each of the links  $\text{R}_2\text{-BDC}$ ,  $\text{R}_3\text{-BDC}$ ,  $\text{R}_4\text{-BDC}$ ,  $\text{R}_5\text{-BDC}$ ,  $\text{R}_6\text{-BDC}$ ,  $\text{R}_7\text{-BDC}$ , 2,6-NDC, BPDC, HPDC, PDC, and TPDC instead of BDC yielded IRMOF-2-16, including the non-interpenetrating structures of BPDC, HPDC, PDC, and TPDC. See Figs. 53A - 53L. It is preferred that the solvent used to  
30   synthesize the IRMOFs be  $\text{N,N}'$ -diethylformamide (DEF) or combined with other

solvents such as alcohols and the like. IRMOFs may also be made using any formamide derivatives, eg. N, N'-R<sub>2</sub>formamide (R may be an alkane, alkene, and the like) as a predominant solvent or mixed.

Each member of the IRMOF series has been isolated and subsequently formulated by chemical microanalysis and single crystal X-ray diffraction studies. All IRMOFs were formulated as Zn<sub>4</sub>O(Link)<sub>3</sub>•(DEF)<sub>x</sub>. All the intensity data were collected on Bruker SMART CCD diffractometer with a graphite monochromated MoKα (λ = 0.71073 Å) radiation. Structures were solved by direct methods and successive difference Fourier syntheses with SHELXTL software package. Final R1 values were calculated with  $I > 2\sigma(I)$ .

Crystal data for:

IRMOF-2: cubic, space group *Fm-3m*,  $a = 25.772(1)$  Å,  $V = 17117(1)$  Å<sup>3</sup>,  $Z = 8$ ,  $R1 = 0.0976$ .

IRMOF-3: cubic, *Fm-3m*,  $a = 25.747(1)$  Å,  $V = 17067(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $R1 = 0.1160$ .

IRMOF-4: cubic, *Fm-3m*,  $a = 25.849(1)$  Å,  $V = 17272(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $R1 = 0.0706$ .

IRMOF-5: cubic, *Pm-3m*,  $a = 12.882(1)$  Å,  $V = 2137.6(3)$  Å<sup>3</sup>,  $Z = 1$ ,  $R1 = 0.1181$ .

IRMOF-6: cubic, *Fm-3m*,  $a = 25.842(2)$  Å,  $V = 17258(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $R1 = 0.1325$ .

IRMOF-7: cubic, *Pm-3m*,  $a = 12.914(3)$  Å,  $V = 2153.9(7)$  Å<sup>3</sup>,  $Z = 1$ ,  $R1 = 0.1957$ .

IRMOF-8: cubic, *Fm-3m*,  $a = 30.092(2)$  Å,  $V = 27248(3)$  Å<sup>3</sup>,  $Z = 8$ ,  $R1 = 0.1691$ .

IRMOF-9: orthorhombic,  $a = 17.147(1)$  Å,  $b = 23.322(1)$  Å,  $c = 25.255(1)$  Å,  $V = 10099.6(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $R1 = 0.0802$ .

IRMOF-10: It was not possible to obtain single crystals of sufficient quality to perform an X-ray single crystal analysis study. However, its observed X-ray powder diffraction pattern was the same as that observed for IRMOF-12 (below), and

it was confirmed by a simulated pattern for IRMOF-10 based on IRMOF-12 coordinates: cubic,  $Fm-3m$ ,  $a = 34.281(2) \text{ \AA}$ ,  $V = 40286(4) \text{ \AA}^3$ ,  $Z = 8$ .

IRMOF-11: trigonal,  $R-3m$ ,  $a = 24.822(1) \text{ \AA}$ ,  $c = 56.734(3) \text{ \AA}$ ,  $V = 30272(3) \text{ \AA}^3$ ,  $Z = 12$ ,  $R1 = 0.0963$ .

5 IRMOF-12: cubic,  $Fm-3m$ ,  $a = 34.281(2) \text{ \AA}$ ,  $V = 40286(4) \text{ \AA}^3$ ,  $Z = 8$ ,  $R1 = 0.1080$ .

IRMOF-13: Same as treatment for IRMOF-10 but using IRMOF-11: Trigonal,  $R-3m$ ,  $a = 24.822(1) \text{ \AA}$ ,  $c = 56.734(3) \text{ \AA}$ ,  $V = 30272(3) \text{ \AA}^3$ ,  $Z = 12$ .

10 IRMOF-14: cubic,  $Fm-3m$ ,  $a = 34.381(13) \text{ \AA}$ ,  $V = 40642(26) \text{ \AA}^3$ ,  $Z = 8$ ,  $R1 = 0.1914$ .

IRMOF-15: cubic,  $Im-3m$ ,  $a = 21.459(1) \text{ \AA}$ ,  $V = 9882(1) \text{ \AA}^3$ ,  $Z = 1$ ,  $R1 = 0.1164$ .

IRMOF-16: cubic,  $Pm-3m$ ,  $a = 21.490(1) \text{ \AA}$ ,  $V = 9925(1) \text{ \AA}^3$ ,  $Z = 1$ ,  $R1 = 0.1845$ .

15 All IRMOFs have the expected topology of  $\text{CaB}_6$  (see M. O'Keeffe and B.G. Hyde, Crystal Structures I : Patterns and Symmetry (Mineralogy Society of America, Washington, DC, 1996)) adapted by the prototype IRMOF-1 (Fig. 37), in which an oxide-centered  $\text{Zn}_4\text{O}$  tetrahedron is edge-bridged by six carboxylates to give the octahedron-shaped SBU that reticulates into a 3-D cubic porous network. However, the IRMOFs differ in the nature of functional groups decorating the pores and in the metrics of their pore structure.

20 In IRMOF-2 to 7, BDC links with bromide, amine, n-propoxy, n-pentoxo, cyclobutyl, and fused benzene functional groups reticulate into the desired structure wherein these groups are now pointing into the voids (Figs. 2 to 7). These results indicate the general nature of the synthetic method and illustrate its amenability to employing a wide variety of carboxylate links having a diversity of functional groups-rare aspects that heretofore remain largely absent in crystalline solid-state and porous materials research. See C.W. Jones, K. Tsuji and M.E. Davis, *Nature* **393**, 52 (1998).

25 Further, the present invention shows that expansion of the pores is also contemplated as being within the purview of the present invention. This is illustrated

30

by the structures of IRMOF-8 to 16 (Figs. 8 to 16), in which progressively longer links have been successfully employed.

Previous geometric analysis of the primitive cubic system showed that expansion of links results in interpenetrating frameworks, sometimes with optimal porosity. See T.M. Reineke, M. Eddaoudi, D. Moler, M. O'Keeffe and O.M. Yaghi, *J. Am. Chem. Soc.* **122**, 4843 (2000). In fact, with the exception of the non-interpenetrating structure involving 2,6-NDC (IRMOF-8) (Fig. 44), each of BPDC, HPDC, PDC and TPDC (respectively, IRMOF-9, 11, 13, and 15; Figs. 9, 11, 13, and 15) are reticulated as doubly interpenetrating structures. However, by carrying out the original reactions under more dilute conditions, non-interpenetrating counterparts have been successfully achieved for all links including TPDC (IRMOF-10, 12, 14, and 16; Figs. 10, 12, 14, and 16); a rare achievement in view of the fact that no strategies have thus far been described for the synthesis of both interpenetrating and non-interpenetrating forms of the same extended structure (Similar behavior has been described for catenated discrete molecules: M. Fujita, *Acc. Chem. Res.* **32**, 53 (1999)).

Comparison of the percent free volume in crystals of IRMOF-1-16 (Fig. 54A) shows that it varies in small increments (1 to 5%) from 55.8% in IRMOF-5 to 91.1% in IRMOF-16. Remarkably, the lowest percent free volume obtained in this series exceeds that found in some of the most open zeolites such as faujasite (see M.J. Bennett, J.V. Smith, *Mater. Res. Bull.* **3**, 633 (1968)) in which the free space is 45-50% of the crystal volume. In fact, the fraction of free space in crystals of the expanded IRMOF series, especially those of IRMOF-8, 10, 12, 14 and 16 has generally only been achievable in non-crystalline porous systems such as SiO<sub>2</sub> xerogels and aerogels. See N. Hüsing, U. Schubert, *Angew. Chem. Int. Ed.* **37**, 22 (1998).

It is worth noting that the calculated crystal densities (in the absence of guests) of these materials also vary in small increments (ca. 0.1) in the range 1.00 g/cm<sup>3</sup> for IRMOF-5 to 0.21 g/cm<sup>3</sup> for IRMOF-16 (Fig. 54B). Moreover, it is remarkable that the densities of IRMOF-8, 10, 12, 14, 15 and 16 are the lowest recorded for any crystalline material known to date. As far as is known, the next lowest density is that of Li metal (0.56 g/cm<sup>3</sup>). The ability to design IRMOFs with low densities below 1 ml/g



and specifically lower than 0.6 ml/g is a clear consequence of the power of isorecticular chemistry.

As expected, the impact of functionalization on pore dimensions is pronounced: relative to IRMOF-1, both the free and fixed diameters of the pores in IRMOF-2 to 7 are modulated downward at approximately 2 Å intervals in the respective ranges, 11.2 to 3.8 Å and 18.6 to 12.8 Å (Fig. 54C). Also, a similar trend is observed for the interpenetrating structures, where pore sizes that fall below those of the IRMOF-1 are obtained. However, all the expanded non-interpenetrating structures have free and fixed diameter values that are much higher, falling within the respective ranges 12.6 to 19.1 Å and 21.4 to 28.8 Å (Fig. 18)--the latter upper limit being in the mesoporous range, indicating the likelihood that such reticular chemistry may be employed more routinely towards the design and synthesis of crystalline and fully-ordered mesoporous crystals.

Given the exceptional attributes of such materials, including their thermal stability, periodicity, the ability to append functional groups in the pores, and the demonstrated systematic variation in pore size and porosity, it is expected that each member of this series would exhibit an unusually rich inclusion chemistry. Results hereinbelow in at least one direction, that of methane storage, provide a glimpse into the vast potential of IRMOFs.

Although methane constitutes one of the most abundant sources of energy on earth, it is the least utilized source of fuel due to the long-standing challenge in its transport and storage at practical temperatures and pressures; conditions believed to be attainable by sorption of methane into porous materials. See V.C. Menon, S. Komaeneni, *J. Porous Mater.* **5**, 43 (1998). Given that IRMOF-6 has an aperture (van der Waals dimension of 5.9 Å) (Van der Waals radius of C (1.70 Å) was employed in determination of distance parameters; Bondi, *A. J. Phys. Chem.* **68**, 441 (1964)) considered to be suitable for methane uptake, the present inventors sought to examine its viability in methane storage.

It was necessary first to study IRMOF-6 using thermal gravimetric and gas sorption techniques to show that its framework has the high porosity and rigidity needed to allow maximum uptake of methane. Thus the chloroform exchanged

IRMOF-6,  $\text{Zn}_4\text{O}(\text{R}_6\text{-BDC})_3 \cdot (\text{CHCl}_3)_7$ , was heated gradually to  $800^\circ\text{C}$  under inert atmosphere. A large and sharp weight loss of 50% of the original sample was observed below  $100^\circ\text{C}$ , which was attributed to liberation of all chloroform guests from the pores (Calcd: 49%) (Fig. 55A). The evacuated framework has a stability range of 100 to  $400^\circ\text{C}$  as evidenced by the fact that no additional weight loss was observed at those temperatures, after which the framework eventually decomposes.

The gas sorption isotherm was measured for IRMOF-6 to show that it has a rigid framework, and that it can maintain its porosity in the absence of guests. An exact amount of the chloroform-exchanged IRMOF-6 was introduced into a microbalance apparatus, and evacuated at room temperature and  $10^{-5}$  torr according to already published protocol. See M. Eddaoudi, H. Li and O.M. Yaghi, *J. Am. Chem. Soc.* **122**, 1391 (2000). All the chloroform guest molecules were removed from the pores, as confirmed by the fact that no additional weight change was observed upon evacuating the sample overnight and heating it to  $150^\circ\text{C}$ .

At this point, the X-ray powder diffraction of the evacuated form of IRMOF-6 was found to be identical to that of the as-synthesized form, indicating the architectural stability of the evacuated framework. Thus, increments of nitrogen gas were introduced into the chamber containing the evacuated framework, at 78 K, and the resulting weight changes after each addition were recorded and plotted (Fig. 55B). This revealed a reversible type I isotherm behavior characteristic of a microporous material. The plateau was reached at relatively low pressure with no additional uptake at relatively medium pressures (near condensation pressure  $P/P_0 \sim 0.5$ ), confirming the homogeneity of the pores.

By applying the Langmuir and DR equations, the Langmuir surface area and pore volume, respectively, were estimated to be  $S_{\text{langmuir}} = 2,630 \text{ m}^2/\text{g}$  and  $V_p = 0.60 \text{ cm}^3/\text{cm}^3$ . Furthermore, the evacuated sample was also exposed to different organic vapors ( $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$  and  $\text{C}_6\text{H}_{12}$ ) to also give type I reversible isotherms (Fig. 55B), and pore volumes that converged to the same values (0.57 to  $0.60 \text{ cm}^3/\text{cm}^3$ ) for all sorbents, further confirmation of the homogeneity of the pores. See S.J. Gregg and K.S.W., Adsorption Surface Area and Porosity, Academic Press, London, UK, 2nd Ed (1982).

The exceptionally high surface area and pore volumes observed for IRMOF-6 coupled with its appropriately designed aperture made it an ideal candidate for methane storage. Indeed, the methane sorption isotherm was measured in the pressure range 0 to 45 atm and room temperature, and found to have an uptake of 240 cm<sup>3</sup>/g (155 cm<sup>3</sup>/cm<sup>3</sup>) at 36 atm (Fig. 55C), which is the highest methane capacity recorded for any crystalline material including zeolite 5A (87 cm<sup>3</sup>/cm<sup>3</sup>) and other coordination frameworks up to (213 cm<sup>3</sup>/g). See V.C. Menon, S. Komaeneni, *J. Porous Mater.* **5**, 43 (1998); K. Seki, *Chem. Commun.* **16**, 1496 (2001); and S. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem., Int. Ed.*, **39**, 2081 (2000).

Based on v/v, the amount of methane sorbed by IRMOF-6 at 36 atm (generally regarded as a substantially safe and cost effective pressure limit), represents 70% of the amount generally stored in laboratory compressed methane cylinders in which significantly higher, less cost effective, and (in certain circumstances) potentially less safe pressure (205 atm) is employed. It is believed that the present invention is an advance which will impact the impending use of these materials in automobile fueling. See U.S. Patent No. 5,862,796, issued to K. Seki et al. on January 26, 1999.

Methane uptake was also evaluated by testing IRMOF-1 and IRMOF-2 under the same conditions where their uptake was found to be lower (135 and 120 cm<sup>3</sup>/cm<sup>3</sup>) than that of IRMOF-6--a significant difference that may be attributable to the hydrophobic nature of H<sub>4</sub>C<sub>2</sub> units in IRMOF-6. Thus, functionalizing the pores with larger hydrocarbons as illustrated in IRMOF-4, 5, and 7, may indeed result in even higher capacities.

To show that the expanded frameworks, for which high free volume and low densities were calculated, can indeed maintain their permanent porosity in the absence of guests, the present inventors examined some of their sorption isotherms. It was indeed found that some of the most open members of this series (IRMOF-12 and 14) are porous, in that they exhibit behavior similar to that described above for IRMOF-6. In addition, they maintain their crystallinity in the absence of guests as evidenced by coincidence of the X-ray powder diffraction patterns of the as-synthesized material with those measured for the evacuated form of each of IRMOF-12 and 14 (Fig. 55D).

Prior to the present invention, the assembly of extended structures in a deliberate manner has been limited to hydrogen bonded guanidinium-sulfonate networks (V.A. Russell, C.C. Evans, W.J. Li and M.D. Ward, *Science* **276**, 575 (1997)), and frameworks based on silver and nitrogen donor links (Y.H. Kiang, G.B. Gardner, S. Lee, Z.T. Xu and E.B. Lobkovsky, *J. Am. Chem. Soc.* **121**, 8204 (1999)). In contrast, the present invention provides a unique approach that succeeds in the assembly of pre-designed rigid skeletal backbone structure and in imparting functionality and metric variation onto its pores, ultimately leading to functional materials capable of high uptake of gases and organic vapors. The intrinsic value of this design approach lies in the ability to control and direct the outcome of molecular assembly of extended networks. It is believed that the present invention ushers a new era in solid-state synthesis.

To further illustrate the inventive IRMOFs and methods for making them, the following examples are given. It is to be understood that these examples are provided for illustrative purposes and are not to be construed as limiting the scope of the present invention.

## EXAMPLES

### Preparation of IRMOF-1:

**Method 1:** 1,4-benzenedicarboxylic acid, H<sub>2</sub>BDC, (0.070 g, 0.42 mmol) and zinc nitrate hexahydrate, Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O, (0.250 g, 0.84 mmol) were dissolved in 10mL dimethylformamide, DMF. Then, 0.10 ml of hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, (30% aqueous) was added, followed by the addition of 0.10 mL of 50 times diluted dimethylamine (DMA) (40% aqueous) in DMF. The resultant mixture was diluted again 10 times with DMF. After several days (~7-10 days), a pure phase IRMOF-1 was formed.

In Figure 1, a representation of a {100} layer of the IRMOF-1 framework is shown along the *a*-axis (C = grey; O = green). The ZnO<sub>4</sub> tetrahedra are indicated in purple. The frameworks interconnect to form a 3-D stable, porous crystalline structure.

The purity of the as-synthesized compound was confirmed by X-ray powder diffraction (XRPD) pattern as shown in **Figure 2a**.

**Method 2:** 1,4-benzenedicarboxylic acid, H<sub>2</sub>BDC, (0.033 g, 0.20 mmol) and zinc nitrate tetrahydrate, Zn(NO<sub>3</sub>)<sub>2</sub>•4H<sub>2</sub>O, (0.156 g, 0.60 mmol) were dissolved in

5 ml diethylformamide (DEF) and left at room temperature. After one week, the desired compound IRMOF-1 was formed in high yield (~85%). The purity of the as-synthesized compound was confirmed by X-ray powder diffraction (XRPD) pattern as shown in **Figure 2b**.

5                   **Method 3:** An exact amount of 1,4-benzenedicarboxylic acid, H<sub>2</sub>BDC, (0.033 g, 0.20 mmol) and zinc nitrate tetrahydrate, Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, (0.156 g, 0.60 mmol) was dissolved in 5 ml diethylformamide, DEF, and placed in a Parr Teflon-lined stainless steel vessel (23 mL). The vessel was sealed and heated at a constant rate 2°C/min to 105°C for 20 h and then cooled to room temperature at a rate of 1°C/min. 10 The resultant compound was a pure IRMOF-1 as confirmed by X-ray powder diffraction (XRPD) pattern as shown in **Figure 2c**.

Preparation of IRMOF-2:

Exact amount of 2-bromobenzenedicarboxylic acid, (o-BrBDCH<sub>2</sub>) (0.040 g, 0.160 mmol), and zinc nitrate tetrahydrate, Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, (0.156 g, 0.20 15 mmol), were dissolved in 15 mL diethylformamide, DEF, and placed in a Parr Teflon-lined stainless steel vessel (23 mL). The vessel was sealed and heated at a constant rate (2°C/min) to 95°C for 20 h and then cooled to room temperature at a rate of 1°C/min. The resultant sample (67%) was filtered and washed with DEF (3 x 5mL) yielding IRMOF-2.

20                   **Elemental analysis:** C<sub>59</sub>H<sub>86</sub>Br<sub>3</sub>O<sub>20</sub>N<sub>7</sub>Zn<sub>4</sub> = Zn<sub>4</sub>O(o-BrBDC)<sub>3</sub>·(DEF)<sub>7</sub>  
Calcd C, 41.33; H, 5.06; N, 5.72. **Found C, 41.23; H, 5.28; N, 5.59.**

**FT-IR** (KBr, 3500-400 cm<sup>-1</sup>): 3455 (br), 2982 (m), 2940 (w), 2874(w), 1668 (vs), 1647 (s), 1622 (s), 1556(w), 1485(m), 1449 (s), 1387 (vs), 1260 (m), 1214 (m), 1118 (w), 1042 (w), 827 (w), 776 (w), 741 (w), 665 (w), 542(w).

25                   Preparation of IRMOF-3:

Zn<sub>4</sub>O(H<sub>2</sub>NBDC)<sub>3</sub>·(DEF)<sub>x</sub> (IRMOF-3): A mixture of diethylformamide and ethanol DEF/C<sub>2</sub>H<sub>5</sub>OH : 9/3 ml containing 2-amino 1,4 benzenedicarboxylic acid, H<sub>2</sub>BDCNH<sub>2</sub>, (0.036 g, 0.20 mmol) and zinc nitrate tetrahydrate, Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, (0.156 g, 0.60 mmol) was placed in a Parr Teflon-lined stainless steel vessel (23 mL). The vessel was sealed and heated at a constant 30 rate 2°C/min to 105°C for 20 h and then cooled to room temperature at a constant



rate of 1° C/min. The resultant product, IRMOF-3 (90%) was filtered and washed with DEF/ethanol mixture (3 x 5mL).

IRMOF-3 is insoluble in water and all common organic solvents such as ethanol, acetonitrile, tetrahydrofuran, chloroform, dichloromethane, acetone, N,N'-dimethylformamide, and N,N'-diethylformamide.

Phase purity of the bulk products was confirmed by comparison of the observed X-ray powder diffraction (XRPD) pattern shown in **Figure 4a**, and the calculated X-ray powder diffraction (XRPD) pattern shown in **Figure 4b** simulated from the single-crystal structure data of IRMOF-3.

**Elemental analysis for IRMOF-3:**  $C_{59}H_{92}O_{20}N_{10}Zn_4 = Zn_4O(H_2NBDC)_3 \cdot (DEF)_7$  Calcd C, 46.31; H, 6.04; N, 9.20. Found C, 46.59; H, 6.04; N, 9.24.

**Infra-Red spectra for IRMOF-3 (Figure 5):**

**FT-IR for IRMOF-3 (KBr, 3500-400  $cm^{-1}$ ):** Infrared spectra characteristic peaks 3455 (br), 3338 (br), 2976 (m), 2936 (w), 2879 (w), 1673 (vs), 1571 (s), 1495 (w), 1433 (s), 1387 (vs), 1260 (m), 1214 (m), 1153 (w), 1113 (w), 944 (w), 899 (w), 827 (w), 782 (m), 710 (w), 717 (m), 644 (w), 593 (w), 517 (w).

**Thermogravimetric Analysis for IRMOF-3 (Figure 6):** A

crystalline sample was heated at a constant rate, 5° C/min, under nitrogen flow (20ml/min) from 30 to 700°C. As shown in Figure 6, two weight loss steps were observed below 350°C: the first can be attributed to the loss of free DEF (~ 6 DEF), and the second, occurring between 150 and 350° C, to the desorption of the hydrogen bound DEF. In the last step, occurring between 350 and 500°C, the framework decomposes.

**Preparation of IRMOF-3 with chloroform molecules as guests,**

**$Zn_4O(H_2NBDC)_3 \cdot (CHCl_3)_x$ :** A fresh as-synthesized sample was immersed in chloroform solution. The solution was twice refreshed with chloroform and left overnight for a complete exchange. The exchanged compound conserves its overall integrity as shown by retention of the original XRPD pattern. IR, elemental analysis, and thermal gravimetric analysis confirmed the completion of the exchange as shown by the data below:

**Elemental analysis for  $\text{Zn}_4\text{O}(\text{H}_2\text{NBDC})_3 \cdot (\text{CHCl}_3)_x$ :**

$\text{C}_{30.8}\text{H}_{21.8}\text{O}_{13}\text{N}_3\text{Cl}_{6.8}\text{Zn}_4 = \text{Zn}_4\text{O}(\text{H}_2\text{NBDC})_3 \cdot (\text{CHCl}_3)_{6.8}$  Calcd C, 23.00; H, 1.38; N, 2.65. Found C, 22.92; H, 1.53; N, 2.67.

**FT-IR for  $\text{Zn}_4\text{O}(\text{H}_2\text{NBDC})_3 \cdot (\text{CHCl}_3)_x$  (KBr, 3500-400  $\text{cm}^{-1}$ ) (**Figure 7**):** 3460 (br), 3353 (br), 1571 (s), 1505 (w), 1428 (s), 1383 (vs), 1260 (w), 1163 (w), 950 (w), 893 (w), 837 (w), 802 (w), 717 (m), 705 (w), 675 (w), 588 (w), 522 (w).

The very strong peak at 1673  $\text{cm}^{-1}$  disappeared as expected due to the full exchange of diethylformamide, DEF, with the chloroform.  $\nu_{\text{C=O}}$  (DEF) = 1673  $\text{cm}^{-1}$ .

**Thermogravimetric analysis for  $\text{Zn}_4\text{O}(\text{H}_2\text{NBDC})_3 \cdot (\text{CHCl}_3)_x$  (**Figure 8**):** The exchanged crystalline sample was heated at a constant rate, 5°C/min, under nitrogen flow (20ml/min) from 30 to 760°C. As shown in **Figure 8**, a sharp weight loss was observed below 80°C corresponding to the loss of the chloroform guest molecules (~ 7.2  $\text{CHCl}_3$ ). In the last step, occurring between 380 and 500°C, the framework decomposes.

**Porosity studies for  $\text{Zn}_4\text{O}(\text{H}_2\text{NBDC})_3$  IRMOF-3:**

As observed from thermogravimetric analysis (TGA) the exchanged sample can lose all of the chloroform guest molecules under a flow of nitrogen at a relatively low temperature (~80°C), whereas diethylformamide, DEF, requires higher temperatures for removal. As a consequence, we opted to choose the exchanged framework for the sorption studies.

An exact amount of the exchanged sample,  $\text{Zn}_4\text{O}(\text{H}_2\text{NBDC})_3 \cdot (\text{CHCl}_3)_x$ , was introduced into a Cahn C-1000 microbalance. The compound was evacuated at room temperature and  $P = 10^{-5}$  torr. All the chloroform guest molecules were removed in a short period of time (~15 minutes) as confirmed by no additional weight change upon exposing the sample to vacuum over night or under extended heat (~ 150°C).

To confirm the stability and porosity of the evacuated framework, the nitrogen sorption at 78K was monitored by introducing different increments of nitrogen gas to the sample chamber. As shown in **Figure 9**, the nitrogen sorption isotherm is a Type I isotherm and fully reversible, characteristic of a microporous material (< 2.0 nm). The plateau was reached at relatively low pressure with no

additional uptake at relatively medium pressures (near condensation pressure  $P/P_0 \sim 0.5$ ), confirming the homogeneity of the pores and the absence of any mesoporosity or macroporosity.

By applying the Langmuir and DR equations, the Langmuir surface and pore volume respectively were estimated:  $S_{\text{langmuir}} = 2701 \text{ m}^2/\text{g}$  and  $V_p = 0.58 \text{ cm}^3/\text{cm}^3$ .

The evacuated sample was also exposed to different organic vapors such as dichloromethane  $\text{CH}_2\text{Cl}_2$ , benzene  $\text{C}_6\text{H}_6$ , carbon tetrachloride  $\text{CCl}_4$  and cyclohexane  $\text{C}_6\text{H}_{12}$ . All the resultant isotherms were Type I and reversible as shown in **Figure 10**. The data are summarized in **Table 1**, and they indicate that, regardless of the sorbed guest, the pore volumes converge to the same values (0.52-0.59  $\text{cm}^3/\text{cm}^3$ ): final proof of the homogeneity of the pores.

The resultant cubic IRMOF-3 crystals were collected and fully characterized. The crystallographic parameters and a picture of the framework are summarized in **Figure 3**. The elemental analysis confirms the composition as discussed above, and the Infrared spectrum confirms that the carboxylates are fully deprotonated. The overlap of the observed and simulated XRPD confirms the purity of the sample. Diethylformamide molecules occupied the void spaces in the porous structure of IRMOF-3. The DEF guest molecules can be removed from the pores under extended vacuum or by heating the sample as shown in Figure 6. The DEF guest molecules can also be fully exchanged with a volatile molecule, such as chloroform, as proven by the data above. To confirm that IRMOF-3 maintains its structure and mainly its porosity upon removing the guest molecules, sorption studies were carried out on the fully evacuated IRMOF-3. As shown in Figure 9, the isotherm is a type I isotherm characteristic of a microporous material (Nitrogen sorption isotherm is a universal and powerful tool to characterize porous material). The data summarized in Table 1 prove that IRMOF-3 has homogeneous porosity and is able to sorb different guest molecules. It is believed that the stability of the framework may primarily be due to the stability of the  $\text{M}_4\text{O}(\text{CO}_2)_6$  cluster (secondary building unit).

Preparation of IRMOF-4:

An exact amount of 2,5-propyl-benzenedicarboxylic acid,  $([\text{OC}_3\text{H}_7]_2\text{BDCH}_2)$  (0.032 g, 0.111 mmol), and zinc nitrate tetrahydrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , (0.126 g, 0.48 mmol), were dissolved in 10ml diethylformamide, DEF, placed in a Parr Teflon-lined stainless steel vessel (23 mL). The vessel was sealed and heated at a constant rate (2°C/min) to 95°C for 36 h and then cooled to room temperature at a rate of 1°C/min. The resultant sample was filtered and washed with DEF (3 x 5mL) yielding IRMOF-4.

**Elemental analysis:**  $\text{C}_{77}\text{H}_{125}\text{O}_{26}\text{N}_7\text{Zn}_4 = \text{Zn}_4\text{O}(\text{BrBDC})_3 \cdot (\text{DEF})_7$   
 Calculated C, 50.64; H, 6.90; N, 5.37. **Found C, 50.79; H, 7.20; N, 5.61.**

**FT-IR** (KBr, 3500-400  $\text{cm}^{-1}$ ): 3455 (br), 2976 (m), 2941 (w), 2936 (w), 2879 (w), 1663 (s), 1607 (vs), 1495 (w), 1423 (vs), 1494 (w), 1393 (s), 1270 (m), 1210 (m), 1118 (w), 1067 (w), 980 (w), 802 (m), 746 (w), 644 (w), 552 (w).

Preparation of IRMOF-5:

An exact amount of 2,5-pentyl-benzenedicarboxylic acid,  $([\text{OC}_5\text{H}_{11}]_2\text{BDCH}_2)$  (0.044 g, 0.131 mmol), and zinc nitrate tetrahydrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , (0.130 g, 0.50 mmol), were dissolved in 10ml diethylformamide, DEF, and placed in a Parr Teflon-lined stainless steel vessel (23 mL). The vessel was sealed and heated at a constant rate (2°C/min) to 95°C for 36 h and then cooled to room temperature at a rate of 1°C/min. The resultant sample was filtered and washed with DEF (3 x 5mL) yielding IRMOF-5.

**Elemental analysis:**  $\text{C}_{71}\text{H}_{111}\text{O}_{24}\text{N}_5\text{Zn}_4 = \text{Zn}_4\text{O}([\text{OC}_5\text{H}_{11}]_2\text{BDC})_3 \cdot (\text{DMF})_1(\text{DEF})_4$  Calculated C, 50.75; H, 6.86; N, 4.21.  
**Found C, 50.04; H, 6.86; N, 4.21.**

**FT-IR** (KBr, 3500-400  $\text{cm}^{-1}$ ): 3445 (br), 2961 (m), 2931 (m), 2865 (w), 1658(s), 1607 (vs), 1495 (w), 1429 (vs), 1388 (s), 1281 (w), 1200 (m), 1052 (w), 1006 (w), 904 (w), 807 (m), 761 (w), 731 (w), 665 (w), 552 (w).

Preparation of IRMOF-6:

$\text{Zn}_4\text{O}([\text{C}_2\text{H}_4]\text{BDC})_3 \cdot (\text{DEF})_x$  (IRMOF-6) : cyclobutene 1,4-benzenedicarboxylic acid,  $\text{H}_2\text{BDC}[\text{C}_2\text{H}_4]$ , (0.045 g, 0.20 mmol) and zinc nitrate tetrahydrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , (0.156 g, 0.60 mmol) were dissolved in 12mL diethylformamide, DEF and placed in a Parr Teflon-lined stainless steel vessel (23

mL). The vessel was sealed and heated at a constant rate (2°C/min) to 105°C for 20 h and then cooled to room temperature at a rate of 1°C/min. The resultant sample (92%), IRMOF-2, was filtered and washed with DEF (3 x 5mL). It is insoluble in water and all common organic solvents such as ethanol, acetonitrile, tetrahydrofuran, chloroform, dichloromethane, acetone, N,N'-dimethylformamide, and N,N'-diethylformamide.

Phase purity of the bulk product was confirmed by comparison of the observed X-ray powder diffraction (XRPD) pattern, shown in **Figure 12a**, and the calculated X-ray powder diffraction pattern, shown in **Figure 12b**, simulated from the single-crystal structure data of IRMOF-2,  $\text{Zn}_4\text{O}([\text{C}_2\text{H}_4]\text{BDC})_3 \cdot (\text{DEF})_x$ .

**Elemental analysis for IRMOF-6:**  $\text{C}_{57.5}\text{H}_{78.5}\text{O}_{18.5}\text{N}_{5.5}\text{Zn}_4 = \text{Zn}_4\text{O}([\text{C}_2\text{H}_4]\text{BDC})_3 \cdot (\text{DEF})_{5.5}$  Calculated C, 46.77; H, 5.22; N, 5.86. **Found C, 46.75; H, 5.45; N, 5.19.**

**Infra-Red spectra for IRMOF-6 (Figure 13):**

FT-IR for IRMOF-6 (KBr, 3500-400  $\text{cm}^{-1}$ ): 3419 (br), 2976 (m), 2936 (m), 2365 (w), 2340 (w), 1668 (s), 1605 (vs), 1489 (m), 1398 (vs), 1303 (w), 1265 (w), 1112 (w), 941 (w), 812 (m), 782 (m), 735 (w), 542 (m).

**Thermogravimetric Analysis for IRMOF-6 (Figure 14):** A

crystalline sample was heated at a constant rate (5°C/min) under nitrogen flow (20ml/min) from 30 to 700°C. As shown in Figure 14, two weight loss steps were observed below 400°C: the first can be attributed to the loss of DEF at the crystal surface (~ 1.65 DEF), and the second, occurring between 100 – 200°C, to the desorption of DEF guest molecules. In the last step, 400-500°C, the framework decomposes.

**Preparation of IRMOF-6 with chloroform molecules as guests,**

$\text{Zn}_4\text{O}([\text{C}_2\text{H}_4]\text{BDC})_3 \cdot (\text{CHCl}_3)_x$ : A fresh as-synthesized sample was immersed in chloroform solution. The solution was refreshed twice with chloroform and left overnight for a complete exchange. The exchanged compound conserves its overall integrity as shown by the retention of the original in the XRPD pattern. IR, elemental analysis, and thermal gravimetric analysis confirmed the completion of the exchange as shown by the data below:



**Elemental analysis for  $\text{Zn}_4\text{O}([\text{C}_2\text{H}_4]\text{BDC})_3 \cdot (\text{CHCl}_3)_x$ :**

$\text{C}_{36.8}\text{H}_{24.8}\text{O}_{13}\text{Cl}_{6.8}\text{Zn}_4 = \text{Zn}_4\text{O}([\text{C}_2\text{H}_4]\text{BDC})_3 \cdot (\text{CHCl}_3)_{6.8}$  Calcd C, 26.61; H, 1.50; N, 0.00. **Found C, 26.63; H, 1.55; N, 0.00.**

**FT-IR for  $\text{Zn}_4\text{O}([\text{C}_2\text{H}_4]\text{BDC})_3 \cdot (\text{CHCl}_3)_x$  (KBr, 3500-400  $\text{cm}^{-1}$ )**

5 (**Figure 15**): 3424 (br), 2936 (br), 1581 (s), 1494 (m), 1398 (vs), 1204 (w), 1143 (w), 1031 (w), 940 (w), 817 (w), 777 (w), 746 (w), 537 (w). The very strong peak at 1668  $\text{cm}^{-1}$  disappeared as expected due to the full exchange of DEF with the Chloroform.  $\nu_{\text{C=O}}$  (DEF) = 1668  $\text{cm}^{-1}$ .

**Thermogravimetric analysis for  $\text{Zn}_4\text{O}([\text{C}_2\text{H}_4]\text{BDC})_3 \cdot (\text{CHCl}_3)_x$**

10 (**Figure 16**): The exchanged crystalline sample was heated at a constant rate (5°C/min) under nitrogen flow (20ml/min) from 30 to 760°C. As shown in Figure 2b, a sharp weight loss was observed below 80°C, corresponding to the loss of the chloroform guest molecules (~ 6.8  $\text{CHCl}_3$ ) followed by a flat plateau synonym of framework stability up ~ 400°C. In the last step, 400-500°C, the framework  
15 decomposes.

**Porosity studies on IRMOF-6:** As observed from TGA analysis, the exchanged sample can lose all chloroform guest molecules under a flow of nitrogen at relatively low temperature (~80°C) whereas the DEF guests require higher temperatures for removal. As a consequence, we opted to choose the exchanged  
20 framework for the sorption studies.

An exact amount of exchanged sample was introduced into a Cahn C-1000 microbalance. The compound was evacuated at room temperature and  $P = 10^{-5}$  torr. All the chloroform guest molecules were removed in a short time (~15 minutes), as confirmed by no additional weight change upon exposing the sample to  
25 vacuum overnight or under extended heat (~ 150°C).

To confirm the stability and porosity of the evacuated framework, the nitrogen sorption at 78K was monitored by introducing different increments of nitrogen gas to the sample chamber. As shown in **Figure 17**, the sorption isotherm is a Type I isotherm and fully reversible, characteristic of a microporous material (<  
30 2.0nm). The plateau was reached at relatively low pressure with no additional uptake at relatively medium pressures (near condensation pressure  $P/P_0 \sim 0.5$ ),

confirming the homogeneity of the pores, and the absence of mesopores and macropores.

By applying the Langmuir and DR equations, the Langmuir surface and pore volume, respectively, were estimated to be  $S_{\text{langmuir}} = 2630 \text{ m}^2/\text{g}$  and  $V_p = 0.60 \text{ cm}^3/\text{cm}^3$ .

The evacuated sample was also exposed to different organic vapors ( $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$  and  $\text{C}_6\text{H}_{12}$ ) and all the isotherms were Type I and reversible. The data are summarized in **Table 2**, and they show that the pore volume converge to the same values ( $0.57\text{-}0.60 \text{ cm}^3/\text{cm}^3$ ), proving the homogeneity of the pores.

The resultant IRMOF-6 cubic crystals were collected and fully characterized. The crystallographic parameters and a representative picture of the framework are summarized in **Figure 11**. The elemental analysis confirms the composition as shown above, the Infrared confirms that the carboxylates are fully deprotonated. The overlap of the observed and simulated XRPD confirms the purity of the sample. Diethylformamide molecules occupied the void spaces in the porous structure of IRMOF-6. The DEF guest molecules can be removed from the pores under extended vacuum or by heating the sample as shown in Figure 14. The DEF guest molecules can also be fully exchanged with a volatile, molecule such as chloroform as proven by the data above. To confirm that IRMOF-6 maintains its structure and mainly its porosity upon removing the guest molecules sorption studies were carried out on the fully evacuated IRMOF-6. As shown in Figure 17, the isotherm is a type I isotherm characteristic of a microporous material. The data summarized in table 2 prove that IRMOF-6 has homogeneous porous and able to sorb different guests molecules.

#### Preparation of IRMOF-7:

$\text{Zn}_4\text{O}(\text{2,4NDC})_3 \cdot (\text{DEF})_x$  (IRMOF-7) : An exact amount of 2,4 naphthalene dicarboxylic acid, (2,4 H2NDC) (0.015 g, 0.072 mmol), and zinc nitrate tetrahydrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , (0.053 g, 0.20 mmol), were dissolved in 5mL diethylformamide, DEF, and placed in a Parr Teflon-lined stainless steel vessel (23 mL). The vessel was sealed and heated at a constant rate ( $2^\circ\text{C}/\text{min}$ ) to  $85^\circ\text{C}$  for 20 h and then cooled to room temperature at a rate of  $1^\circ\text{C}/\text{min}$ . The resultant sample was

filtered and washed with DEF (3 x 5mL) yielding IRMOF-7. IRMOF-7 is insoluble in water and all common organic solvents such as ethanol, acetonitrile, tetrahydrofuran, chloroform, dichloromethane, acetone, N,N'-dimethylformamide, and N,N'-diethylformamide. The observed X-ray powder diffraction pattern shown in **Figure 19a** was compared to the simulated one in **Figure 19b** to confirm the purity of the as-synthesized IRMOF-7,  $\text{Zn}_4\text{O}(\text{2,4NDC})_3 \cdot (\text{DEF})_x$ .

The resultant IRMOF-7 cubic crystals were collected. The crystallographic parameters and a representative picture are summarized in **Figure 18**.

**Elemental analysis:**  $\text{C}_{71}\text{H}_{101}\text{O}_{23}\text{N}_7\text{Zn}_4 = \text{Zn}_4\text{O}(\text{1,4NDC})_3 \cdot (\text{DEF})_7(\text{H}_2\text{O})_3$  Calcd C, 50.69; H, 6.05; N, 5.83. **Found C, 50.81; H, 6.28; N, 5.85.**

**FT-IR** (KBr, 3500-400  $\text{cm}^{-1}$ ): 3435 (br), 2980 (w), 2935 (w), 2340 (w), 1644 (s), 1605 (vs), 1519 (m), 1466 (m), 1413 (s), 1361 (vs), 1263 (m), 1220 (w), 1163 (w), 1108 (w), 840 (w), 792 (w), 562 (w).

**Preparation of IRMOF-8:**

Exact amounts of 2,6-naphthalene dicarboxylic acid, (2,6 H2NDC) (0.012 g, 0.055 mmol), and zinc nitrate tetrahydrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , (0.110 g, 0.42 mmol), were dissolved in 10ml DEF and left at room temperature. After 2 days, cubic-like crystals were grown. The resultant sample (83%) was filtered and washed with DEF (3 x 5mL), yielding IRMOF-8. Heating the same amounts of starting materials to 95°C for 20hours leads to the same compound. However the crystals made at room temperature have cleaner surfaces and were used for single X-ray data collection.

IRMOF-8 is insoluble in water and all common organic solvents such as ethanol, acetonitrile, tetrahydrofuran, chloroform, dichloromethane, acetone, N,N'-dimethylformamide, and N,N'-diethylformamide. The observed X-ray powder diffraction pattern is shown in **Figure 20**.

**Elemental analysis:**  $\text{C}_{66}\text{H}_{84}\text{O}_{19}\text{N}_6\text{Zn}_4 = \text{Zn}_4\text{O}(\text{NDC})_3 \cdot (\text{DEF})_6$  Calcd C, 51.91; H, 5.54; N, 5.50. **Found C, 51.90; H, 5.96; N, 5.57.**

**FT-IR** (KBr, 3500-400  $\text{cm}^{-1}$ ): 3455 (br), 2982 (m), 2941 (w), 2874

(w), 1667 (s), 1642(m), 1622 (s), 1413 (vs), 1494 (w), 1363 (m), 1266 (m), 1200 (w), 1108 (w), 930 (w), 992 (m), 487 (w).

**Preparation of IRMOF-9:**

**Method 1:** Exact amounts of 4,4'-biphenyldicarboxylic acid, (4,4'-BPDCH<sub>2</sub>) (0.08 g, 0.05 mmol), and zinc nitrate tetrahydrate, Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, (0.110 g, 0.42 mmol), were dissolved in 9ml DEF and placed in a Parr Teflon-lined stainless steel vessel (23 mL). The vessel was sealed and heated at a constant rate (2°C/min) to 85°C for 20 h and then cooled to room temperature at a rate of 1°C/min. The resultant sample (63%) was filtered and washed with DEF (3 x 5mL) yielding IRMOF-9.

**Elemental analysis:** C<sub>73</sub>H<sub>103</sub>O<sub>26</sub>N<sub>9</sub>Zn<sub>4</sub> = Zn<sub>4</sub>O(BPDC)<sub>3</sub>·(DEF)<sub>2</sub>(DMF)<sub>7</sub>(H<sub>2</sub>O)<sub>4</sub> Calcd C, 49.14; H, 5.82; N, 7.07. **Found C, 49.52; H, 6.50; N, 7.22.**

**FT-IR** (KBr, 4000-400 cm<sup>-1</sup>): 3430 (br), 2981 (w), 2935 (w), 2870 (w), 1663 (vs), 1607 (vs), 1545 (m), 1403 (vs), 1347 (s), 1311 (w), 1265 (w), 1220 (w), 1184 (w), 1113 (w), 1011 (w), 777 (m), 705 (w), 680 (w), 644 (w), 456 (w).

**Method 2:** A mixture of N,N'-dimethylformamide and benzene DMF/2-C<sub>3</sub>H<sub>8</sub>OH : 4/4 ml containing 4, 4' biphenyl dicarboxylic acid, H<sub>2</sub>BPDC, (0.015 g, 0.062 mmol) and zinc nitrate tetrahydrate, Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, (0.130 g, 0.50 mmol) was placed in a Parr Teflon-lined stainless vessel (23 mL). The vessel was sealed and heated to 85 °C for 24 h at a rate of 2.0 °C/min and cooled to room temperature at a rate of 2.0 °C/min. The resultant product was filtered, washed with a DMF/benzene mixture (3 x 5mL) to give 60% of IRMOF-9. The as-synthesized IRMOF-9 is insoluble in water and all common organic solvents such as ethanol, acetonitrile, tetrahydrofuran, chloroform, dichloromethane, acetone, N,N'-dimethylformamide, and N,N'-diethylformamide. The observed X-ray powder diffraction pattern is shown in **Figure 22a**, and the simulated pattern from the single X-Ray data is shown in **Figure 22b**.

**Zn<sub>4</sub>O(BPDC)<sub>3</sub>·(DMF)<sub>x</sub> (IRMOF-9) :** A mixture of N,N'-dimethylformamide and benzene DMF/2-C<sub>3</sub>H<sub>8</sub>OH : 4/4 ml containing 4, 4' biphenyl dicarboxylic acid, H<sub>2</sub>BPDC, (0.015 g, 0.062 mmol) and zinc nitrate

tetrahydrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , (0.130 g, 0.50 mmol) was placed in a Parr Teflon-lined stainless vessel (23 mL). The vessel was sealed and heated to 85 °C for 24 h at a rate of 2.0 °C/min and cooled to room temperature at a rate of 2.0 °C/min. The resultant product was filtered, washed with a DMF/benzene mixture (3 x 5mL) to give 60% of IRMOF-9. The as-synthesized IRMOF-9 is insoluble in water and all common organic solvents such as ethanol, acetonitrile, tetrahydrofuran, chloroform, dichloromethane, acetone, N,N'-dimethylformamide, and N,N'-diethylformamide. The observed X-ray powder diffraction pattern is shown in **Figure 22a**, and the simulated pattern from the single X-Ray data is shown in **Figure 22b**.

10                   **The InfraRed spectrum for IRMOF-9** is shown in Figure 23. FT-IR for IRMOF-9: FT-IR (KBr, 4000-400  $\text{cm}^{-1}$ ): 3430 (br), 2936 (w), 1658 (m), 1612 (s), 1541 (w), 1505 (w), 1403 (vs), 1261 (w), 1184 (w), 1108 (w), 1016 (w), 863 (w), 848 (w), 802 (w), 772 (m), 711 (w), 685 (w), 588 (br), 461 (w).

15                   The resultant IRMOF-9 cubic crystals were collected and characterized. The crystallographic parameters and a representative picture of the framework are summarized in **Figure 21**.

Preparation of IRMOF-10:

20                   Exact amounts of 4,4'-biphenyldicarboxylic acid, (4,4'-BPDCH<sub>2</sub>) (0.005 g, 0.02 mmol), and zinc nitrate tetrahydrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , (0.031 g, 0.12 mmol), were dissolved in 16ml DEF and placed in a Parr Teflon-lined stainless steel vessel (23 mL). The vessel was sealed and heated at a constant rate (2°C/min) to 85°C for 20 h and then cooled to room temperature at a rate of 1°C/min. The resultant sample (52%) was filtered and washed with DEF (3 x 5mL) yielding IRMOF-10.

25                   **Elemental analysis:**  $\text{C}_{102}\text{H}_{158}\text{O}_{26}\text{N}_{12}\text{Zn}_4 = \text{Zn}_4\text{O}(\text{BPDC})_3 \cdot (\text{H}_2\text{O})(\text{DEF})_{12}$  Calcd C, 54.94; H, 7.14; N, 7.54. **Found C, 54.40; H, 7.32; N, 7.54.**

30                   **FT-IR** (KBr, 3500-400  $\text{cm}^{-1}$ ): 3455 (br), 2981 (m), 2941 (w), 2880 (w), 1668 (vs), 1607 (vs), 1546 (m), 1398 (s), 1311 (w), 1265 (m), 1220 (m), 1118 (w), 1011 (w), 950 (w), 827 (w), 777 (m), 690 (w), 556 (w).

Preparation of IRMOF-11:



**Method 1:** Exact amounts of tetrahydropyrene-2,7-dicarboxylic acid, (4,4'-HPDCH<sub>2</sub>) (0.015 g, 0.05 mmol), and zinc nitrate tetrahydrate, Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, (0.052 g, 0.20 mmol), were dissolved in 10 ml DEF and placed in a Parr Teflon-lined stainless steel vessel (23 mL). The vessel was sealed and heated at a constant rate (2°C/min) to 105°C for 20 h and then cooled to room temperature at a rate of 1°C/min. The resultant sample (76%) was filtered and washed with DEF (3 x 5mL) yielding IRMOF-11.

**Elemental analysis:** C<sub>114</sub>H<sub>172</sub>N<sub>12</sub>O<sub>27</sub>Zn<sub>4</sub> = Zn<sub>4</sub>O(HPDC)<sub>3</sub>·(DEF)<sub>12</sub>(H<sub>2</sub>O)<sub>2</sub> Calcd C, 56.95; H, 7.21; N, 6.99. **Found C, 56.66; H, 7.02; N, 7.02.**

**FT-IR** (KBr, 4000-400 cm<sup>-1</sup>): 3430 (br), 2977 (w), 2941 (w), 2890 (w), 2840 (w), 1647 (vs), 1601 (s), 1548 (m), 1464 (m), 1398 (vs), 1352 (s), 1301 (w), 1270 (w), 1245 (w), 1214 (w), 1113 (w), 1091 (w), 1006 (w), 827 (w), 650 (w).

**Method 2:** Zn<sub>4</sub>O(TPDC)<sub>3</sub>·4H<sub>2</sub>O·9DMF (**IRMOF-11**) : A mixture of dimethylformamide and isopropanol DMF/2-C<sub>3</sub>H<sub>8</sub>OH : 6/2 ml containing tetrahydropyrene-2,7-dicarboxylic acid, H<sub>2</sub>TPDC (0.015 g, 0.051 mmol), and zinc nitrate tetrahydrate, Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.080 g, 0.31 mmol), was placed in a Parr Teflon-lined stainless vessel (23 mL). The vessel was sealed and heated to 85 °C for 24 h at a rate of 2.0 °C/min and cooled to room temperature at a rate of 2.0 °C/min. The resultant product, rectangular, pale yellow crystals, was filtered, washed with a DMF and isopropanol mixture (3 x 5mL) to yield 69% of IRMOF-11. The as-synthesized IRMOF-11 is insoluble in water and all common organic solvents such as ethanol, acetonitrile, tetrahydrofuran, chloroform, dichloromethane, acetone, N,N'-dimethylformamide, and N,N'-diethylformamide. Phase purity of the bulk products was confirmed by comparison of the observed X-ray powder diffraction pattern shown in **Figure 28a**, and the calculated X-ray powder diffraction pattern shown in **Figure 28b** simulated from the single-crystal structure data of IRMOF-11.

**Elemental analysis for IRMOF-11:** C<sub>81</sub>H<sub>107</sub>N<sub>9</sub>O<sub>26</sub>Zn<sub>4</sub> = Zn<sub>4</sub>O(TPDC)<sub>3</sub>·(4H<sub>2</sub>O)·(9DMF) Calcd C, 51.63; H, 5.72; N, 6.69. **Found C, 51.95; H, 5.53; N, 6.76.**

**Infra-Red spectra for IRMOF-11 (Figure 29):**

**FT-IR for IRMOF-11** (KBr, 4000-400  $\text{cm}^{-1}$ ): 3450 (br), 2934 (w), 2895 (w), 2836 (w), 1677 (vs), 1605 (s), 1552 (m), 1499 (w), 1466 (w), 1433 (s), 1398 (vs), 1347 (s), 1302 (w), 1250 (w), 1091 (w), 1065 (w), 1012 (w), 913 (w), 867 (w), 795 (w), 756 (w), 663 (w), 551 (w)

5                    **Thermogravimetric analysis for IRMOF-11:** A crystalline sample (16.527 mg) was heated from 30 °C to 900 °C at 5.0 °C/min; two separate weight-loss steps were observed. The first weight loss (38.1 %) step at 250 °C corresponds to the removal of (4H<sub>2</sub>O + 9DMF) and the second, which occurs above 400 °C (41.8 %), corresponds to framework decomposition. A plateau between 250 – 400 °C was  
10 observed, confirming the stability of the evacuated framework IRMOF-11 up to 400 °C.

The resultant IRMOF-11 cubic crystals were collected and fully characterized. The crystallographic parameters and a representative picture of the framework are summarized in **Figure 27**. The elemental analysis confirms the  
15 composition as shown above, the Infrared confirms that the carboxylates are fully deprotonated. The overlap of the observed and simulated XRPD confirms the purity of the sample.

Preparation of IRMOF-12:

20                    **Method 1:** Exact amounts of tetrahydropyrene-2,7-dicarboxylic acid, (4,4'-HPDCH<sub>2</sub>) (0.005 g, 0.017 mmol), and zinc nitrate tetrahydrate, Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, (0.031 g, 0.12 mmol), were dissolved in 16mL DEF and placed in a Parr Teflon-lined stainless steel vessel (23 mL). The vessel was sealed and heated at a constant rate (2°C/min) to 85°C for 20 h and then cooled to room temperature at a rate of 1°C/min. The resultant sample (65%) was filtered and  
25 washed with DEF (3 x 5mL) yielding IRMOF-12.

**Elemental analysis:** C<sub>104</sub>H<sub>148</sub>O<sub>24</sub>N<sub>10</sub>Zn<sub>4</sub> = Zn<sub>4</sub>O(HPDC)<sub>3</sub>·(H<sub>2</sub>O)(DEF)<sub>10</sub> Calcd C, 57.20; H, 6.83; N, 6.41. **Found C, 57.16; H, 7.25; N, 6.53.**

30                    **FT-IR** (KBr, 3500-400  $\text{cm}^{-1}$ ): 3455 (br), 2982 (m), 2941 (m), 2879 (w), 1668 (vs), 1602 (s), 1551 (m), 1464 (m), 1434 (m), 1393 (vs), 1352 (m), 1306 (w), 1266 (w), 1220 (w), 1113 (w), 920 (w), 827 (w), 797 (m), 761 (m), 650(w).

**Method 2:  $\text{Zn}_4\text{O}(\text{TPDC})_3 \cdot 11\text{H}_2\text{O} \cdot \text{CHP} \cdot \text{chlorobenzene}$  (IRMOF-12)**

Exact amounts of tetrahydropyrene-2,7-dicarboxylic acid,  $\text{H}_2\text{PDC}$ , (0.040 g, 0.048 mmol), and zinc nitrate tetrahydrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , (0.040 g, 0.15 mmol), were dissolved in 1-cyclohexyl-2-pyrrolidinone, CHP, (7.0 mL) and chlorobenzene (3.0 mL). The mixture was exposed to diluted triethylamine solution. The diluted triethylamine solution was prepared by diluting 0.10 mL of the stock solution (triethylamine : chlorobenzene = 1 : 10, v/v) with 5.0 mL of chlorobenzene. After three weeks cubic, odorless crystals were produced. The resultant product was filtered, washed with a DMF and chlorobenzene mixture (3 x 5 mL) to yield 7% of IRMOF-12. The as-synthesized IRMOF-12 is insoluble in water and all common organic solvents such as ethanol, acetonitrile, tetrahydrofuran, chloroform, dichloromethane, acetone, N,N'-dimethylformamide, and N,N'-diethylformamide. The observed X-ray powder diffraction pattern is shown in **Figure 25a**, and the pattern simulated from the single X-Ray data is shown in **Figure 25b**. Comparison of these two patterns confirms the purity of the as-synthesized IRMOF-12.

**Elemental analysis for IRMOF-12:**

$\text{C}_{70}\text{H}_{80}\text{NO}_{25}\text{ClZn}_4 = \text{Zn}_4\text{O}(\text{TPDC})_3 \cdot (11\text{H}_2\text{O}) \cdot (\text{CHP}) \cdot (\text{chlorobenzene})$  Calcd C, 51.50; H, 4.94; N, 0.86. **Found C, 51.64; H, 3.73; N, 1.01.**

**Infra-Red spectra for IRMOF-12 (Figure 26):**

**FT-IR for IRMOF-12** FT-IR (KBr, 4000-400  $\text{cm}^{-1}$ ): 3434 (br), 3063 (w), 2931 (w), 2890 (w), 2829 (w), 1800 (w), 1581 (s), 1530 (s), 1464 (m), 1429 (s), 1393 (vs), 1352 (s), 1245 (w), 1128 (w), 1082 (w), 1026 (w), 1006 (w), 909 (w), 792 (w), 741 (w), 706 (w), 685 (w), 471 (w).

**Thermogravimetric analysis of IRMOF-12:** A crystalline sample (16.527 mg) was heated from 30 °C to 900 °C at constant rate (5.0 °C/min); two separate weight-loss steps were observed. The first weight loss step (38.1 %) at 250 °C corresponds to the removal of ( $4\text{H}_2\text{O} + 9\text{DMF}$ ) and the second one (41.8 %) to the decomposition of the framework. A pseudo-plateau was observed between 250 °C - 400 °C corresponding to the stability of IRMOF-6 up to 400 °C.

The resultant IRMOF-12 crystals were fully characterized as discussed above. The crystallographic parameters and a representative picture of the

framework are summarized in **Figure 24**. The elemental analysis confirms the composition as shown above, the Infrared confirms that the carboxylates are fully deprotonated. The overlap of the observed and simulated XRPD confirms the purity of the sample.

5 **Preparation of IRMOF-13:**

$\text{Zn}_4\text{O}(\text{PDC})_3 \cdot 4\text{H}_2\text{O} \cdot 6\text{DEF}$  (**IRMOF-13**) : Exact amounts of ppyrene-2,7- dicarboxylic acid,  $\text{H}_2\text{TPDC}$  (0.014g, 0.048 mmol), and zinc nitrate hexahydrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (0.080 g, 0.31 mmol), were dissolved in diethylformamide, DEF, (6.0 mL) and placed in a Parr Teflon-lined stainless vessel  
10 (23 mL). The vessel was sealed and heated to 85 °C for 24 h at a rate of 2.0 °C/min and cooled to room temperature at a rate of 2.0 °C/min.

The resultant product, rectangular, pale yellow crystals, was filtered, washed with a DEF and ethanol mixture (3 x 5mL) to yield 63% of IRMOF-13. The as-synthesized IRMOF-13 is insoluble in water and all common organic solvents  
15 such as ethanol, acetonitrile, tetrahydrofuran, chloroform, dichloromethane, acetone, N,N'-dimethylformamide, and N,N'-diethylformamide. The observed X-ray powder diffraction (XRPD) is shown in **Figure 33**.

**Elemental analysis for IRMOF-13:**  $\text{C}_{84}\text{H}_{98}\text{N}_6\text{O}_{23}\text{Zn}_4 =$   
 $\text{Zn}_4\text{O}(\text{PDC})_3 \cdot (4\text{H}_2\text{O}) \cdot (6\text{DEF})$  Calcd C, 55.40; H, 5.42; N, 4.61. Found C, 55.56; H,  
20 4.85; N, 4.35.

**Infra-Red spectra for IRMOF-13 (Figure 34):**

**FT-IR for IRMOF-13** (KBr, 4000-400  $\text{cm}^{-1}$ ): 3445 (br), 2977 (w), 2936 (w), 2880 (w), 1648 (s), 1612 (s), 1581 (s), 1464 (s), 1393 (vs), 1312 (w), 1261 (m), 1209 (w), 1108 (w), 914 (w), 823 (w), 777 (w), 746 (w), 711 (w), 670 (w), 553 (w).

25 **Thermogravimetric analysis for IRMOF-13:** A crystalline sample (22.256mg) was heated from 25 °C to 700 °C at a constant rate (5.0 °C/min); two separate weight-loss steps were observed. The first weight loss (31.4 %) step below 300 °C corresponds to the removal of ( $4\text{H}_2\text{O} + 6\text{DEF}$ ) and the second one above 420 °C (42.7 %) to the framework decomposition. A pseudo-plateau between 300 - 420  
30 °C was observed, proving the stability of IRMOF-13.

The resultant crystals were collected and fully characterized. The

elemental analysis confirms the composition as shown above, the Infrared confirms that the carboxylates are fully deprotonated, and that expected  $M_4O(CO_2)_6$  cluster is incorporated in structure.

Preparation of IRMOF-14:

5                   **Method 1:** Exact amounts of pyrene-2,7- dicarboxylic acid,  $H_2PDC$  (0.005g, 0.017 mmol), and zinc nitrate hexahydrate,  $Zn(NO_3)_2 \cdot 4H_2O$  (0.031 g, 0.12 mmol), were dissolved in diethylformamide, 16ml, DEF and placed in a Parr Teflon-lined stainless vessel (23 mL). The vessel was sealed and heated to 85 °C for 24 h at a rate of 2.0 °C/min and cooled to room temperature at a rate of 2.0 °C/min.  
10                   The resultant product was filtered, washed with a DEF (3 x 5mL) to yield 70% of IRMOF-14.

**Elemental analysis:**  $C_{84}H_{100}O_{24}N_6Zn_4 = Zn_4O(PDC)_3 \cdot (H_2O)_5(DEF)_6$   
Calcd C, 54.85; H, 5.48; N, 4.57. **Found C, 53.94; H, 5.37; N, 4.72.**

**FT-IR** (KBr, 3500-400  $cm^{-1}$ ): 3455 (br), 2982 (m), 2935 (w), 1658  
15                   (s), 1607 (s), 1581 (m), 1464 (m), 1393 (s), 1261 (m), 1220 (w), 1113 (w), 914 (w),  
827 (m), 751 (w), 711 (w), 511 (w).

**Method 2:**  $Zn_4O(PDC)_3 \cdot 4H_2O \cdot 1/2CHP \cdot 10chlorobenzne$  (**IRMOF-14**): A mixture of dimethylformamide and isopropanol DMF/2- $C_3H_8OH$  : 6/1ml containing pyrene-dicarboxylic acid,  $H_2PDC$  (0.014 g, 0.048 mmol), and zinc nitrate tetrahydrate,  $Zn(NO_3)_2 \cdot 4H_2O$  (0.080 g, 0.31 mmol), was placed in a Parr Teflon-lined stainless vessel (23 mL). The vessel was sealed and heated to 85 °C for 24 h at a rate of 2.0 °C/min and cooled to room temperature at a rate of 2.0 °C/min. The filtrate solution from six vessels (35 mL) was diluted with CHP (1-cyclohexyl-2-pyrrolidinone) (15.0 mL). The final solution was divided equally, transferred into  
20                   five vials, and exposed to diluted triethylamine. The diluted triethylamine solution was prepared by diluting 0.10 mL of the stock solution (triethylamine :  
25                   chlorobenzene = 1 : 10, v/v) with 5.0 mL of chlorobenzene. After two weeks pale brown crystals were produced. The resultant product was filtered, washed with a DMF and chlorobenzene mixture (3 x 5mL) to yield 6% of IRMOF-14. The as-  
30                   synthesized IRMOF-14 is insoluble in water and all common organic solvents such as ethanol, acetonitrile, tetrahydrofuran, chloroform, dichloromethane, acetone,



N,N'-dimethylformamide, and N,N'-diethylformamide. Comparison of the observed X-ray powder diffraction pattern shown in **Figure 31a** and the simulated pattern from the single X-Ray data (**Figure 31b**) confirms the purity of the as-synthesized IRMOF-14.

5                   **Elemental analysis for IRMOF-14:**  $C_{119}H_{90.5}N_{0.5}O_{17.5}Cl_{10}Zn_4 = Zn_4O(PDC)_3 \cdot (4H_2O) \cdot (1/2CHP) \cdot (10chlorobenzene)$  Calcd C, 58.97; H, 3.76; N, 0.29. Found C, 58.68; H, 3.64; N, 0.30.

**Infra-Red spectra for IRMOF-14 (Figure 32):**

10                   FT-IR for IRMOF-14 FT-IR (KBr, 4000-400  $cm^{-1}$ ): 3430 (br), 3048 (w), 2936 (w), 2854 (w), 1607 (m), 1571 (m), 1464 (m), 1393 (vs), 1317 (w), 1261 (m), 1087 (w), 909 (w), 823 (w), 746 (m), 706 (w), 685 (w), 471 (w).

15                   **Thermogravimetric analysis of IRMOF-14:** A crystalline sample (12.000 mg) was heated from 30 °C to 800 °C at 10.0 °C/min; two separate weight-loss steps were observed. The first weight loss (52.4 %) step at 250 °C is attributed to the removal of  $(4H_2O + 1/2CHP + 10chlorobenzene)$  and the second one (34.9 %) to the framework decomposition. A pseudo plateau was observed between 250 - 300 °C indicating the stability of IRMOF-14 up to 300 °C.

20                   The resultant IRMOF-14 crystals, after two weeks, were collected and fully characterized. The crystallographic parameters and a representative picture of the framework are summarized in **Figure 30**. The elemental analysis confirms the composition as shown above, the Infrared confirms that the carboxylates are fully deprotonated. The overlap of the observed and simulated XRPD confirms the purity of the sample.

**Preparation of IRMOF-15:**

25                    $Zn_4O(TPDC)_3 \cdot (DEF)_x$  (IRMOF-15) : Exact amounts of terphenyldicarboxylic acid, H<sub>2</sub>TPDC ( 0.002g, 0.0063mmol), and zinc nitrate hexahydrate,  $Zn(NO_3)_2 \cdot 6(H_2O)$  (0.0075 mg, 0.025 mmol), were dissolved in 1.5 ml diethylformamide (DEF) and placed in a pyrex tube (100mm, 6 ml). The evacuated tube was sealed and heated to 100 °C for 24 h at a rate of 2.0 °C/min and cooled to room temperature at a rate of 0.1 °C/min. The resultant clear cubic crystals were washed with DEF. The X-ray powder diffraction pattern shown in **Figure 35**

30

confirms the homogeneity of the as-synthesized product and is attributed as IRMOF-15.

**Elemental analysis:**  $C_{84}H_{100}O_{24}N_6Zn_4 = Zn_4O(TPDC)_3 \cdot (H_2O)_5(DEF)$   
Calcd C, 55.07; H, 4.05; N, 0.99. **Found C, 55.05; H, 3.80; N, 0.66.**

5

**Infra-Red spectra for IRMOF-15 (Figure 36):**

**FT-IR for IRMOF-15** (KBr, 4000-400  $cm^{-1}$ ): 3451 (br), 2978 (w), 2939 (w), 2877 (w), 1667 (s), 1607 (s), 1545 (w), 1404 (vs), 1393 (vs), 1114 (w), 780 (w).

The resultant IRMOF-15 clear cubic crystals were collected and characterized. The IR data point to the presence of  $M_4O(CO_2)_6$  cluster and therefore coordinated with the observed XRPD for the as-synthesized material assigned as IRMOF-15.

10

Preparation of IRMOF-16

Exact amounts of terphenyldicarboxylic acid,  $H_2TPDC$  (0.004g, 0.0126mmol), and zinc nitrate hexahydrate,  $Zn(NO_3)_2 \cdot 6(H_2O)$  (0.015 mg, 0.05 mmol), were dissolved in 1.0 ml N-methylpyrrolidone (NMP). The solution was diluted with 1 ml diethylformamide (DEF) and placed in a pyrex tube (100mm, 6 ml). The evacuated tube was sealed and heated to 95°C for 24 h at a rate of 2.0°C/min, then to 100°C for 48 h at a constant rate of 2.0°C/min and cooled to room temperature at a rate of 2.0°C/min. The resultant clear cubic crystals was filtered, washed with DEF (3 x 5mL) to yield IRMOF-16.

15

20

**Elemental analysis:**  $C_{145}H_{227}O_{32}N_{17}Zn_4 = Zn_4O(TPDC)_3 \cdot (DEF)_{17}(H_2O)_2$  Calcd C, 58.40; H, 7.99; N, 7.99. **Found C, 58.37; H, 7.97; N, 8.01.**

25

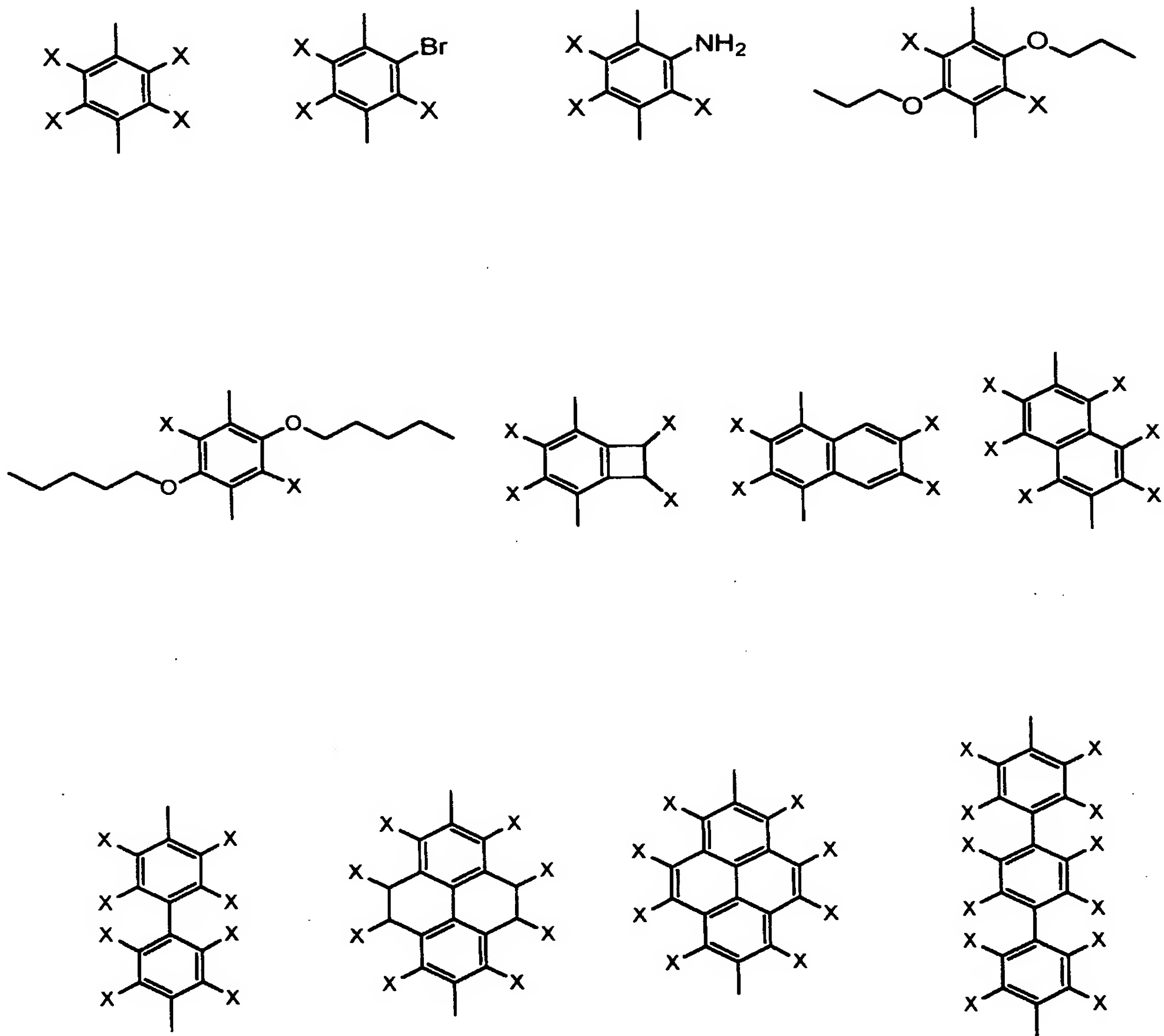
**FT-IR** (KBr, 4000-400  $cm^{-1}$ ): 3425 (br), 2971 (w), 2931 (w), 2880 (w), 1678 (s), 1607 (s), 1409 (s), 1301 9w), 1266 (w), 1118 (w), 1011 (w), 843 (w), 777 (m), 736 (w), 563 (w).

30

While preferred embodiments of the invention have been described in detail, it will be apparent to those skilled in the art that the disclosed embodiments may be modified. Therefore, the foregoing description is to be considered exemplary rather than limiting, and the true scope of the invention is that defined in the following claims.

What is claimed is:

1. An isorecticular metal-organic framework (IRMOF), consisting essentially of:
  - a plurality of secondary building units (SBUs), each of the plurality of SBUs comprising an  $M_4O(CO_2)_6$  cluster; and
  - a compound linking adjacent SBUs, the linking compound comprising a linear ditopic carboxylate having at least one phenyl group and at least one functional group X attached to the at least one phenyl group;wherein the IRMOF has a substantially permanent porosity and is substantially stable.
2. The IRMOF as defined in claim 1 wherein the linking compounds are selected from the group consisting of:



wherein the functional group X is at least one of hydrogen, amines, halides, an R group comprising at least one of linear, substituted or cyclo alkanes ( $\text{CH}_3\text{-(CH}_2\text{)}_n\text{-CH}_2\text{-}$ )  $n=0, 1, 2\ldots$ , alkenes, alkynes, chains, and ether O-R, wherein R is at least one of linear, substituted or cyclo alkanes ( $\text{CH}_3\text{-(CH}_2\text{)}_n\text{-CH}_2\text{-}$ )  $n=0, 1, 2\ldots$ , alkenes, alkynes, chains, and mixtures thereof.

3. The IRMOF as defined in claim 2 wherein X comprises at least one of primary, secondary or tertiary amines; aromatic amines, pyridine, pyrimidine like 5 or 6 membered rings; halides including substituted -RX; alcohols: ROH; thiols: RSH; sulfonates -R-SO<sub>3</sub>; nitro groups -R(NO<sub>2</sub>); phosphates -R-PO<sub>2</sub><sup>-</sup>; epoxides; aldehydes (RCOH); ketones (RCOR); esters RCO<sub>2</sub>R; carboxylic acids; cycloalkenes; cycloalkynes; silyls derivatives; boranes derivatives; ferrocenes, other metallocenes, and mixtures thereof.

4. The IRMOF as defined in claim 1 wherein M in the SBU is a metal cation of a metal chosen from at least one of beryllium, zinc, cadmium, mercury, any of the transition metals in the periodic table, scandium through copper, yttrium through silver, lanthanum through gold, and all known elements from actinium on.

5. A method of forming an isorecticular metal-organic framework (IRMOF), the method comprising the steps of:

dissolving at least one metal salt and at least one linear ditopic carboxylate in a solvent to form a solution under predetermined conditions to produce  $\text{M}_4\text{O}(\text{CO}_2)_6$  *in situ*; and

crystallizing the solution to form the IRMOF.

6. The method as defined in claim 5 wherein the metal salt is formed from a metal cation and an anion, the metal cation being a cation of a metal selected from the group consisting of zinc, cadmium, mercury, and transition metals, and wherein the anion is selected from the group consisting of F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, ClO<sup>-</sup>, ClO<sub>2</sub><sup>-</sup>,



$\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{OH}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{CH}_3\text{CO}_2^-$ ,  $\text{HCO}_2^-$  and  $\text{CF}_3\text{SO}_3^-$ ,  $\text{B}_4\text{O}_7^{2-}$  and  $\text{PF}_6^-$ .

7. The method as defined in claim 6 wherein the at least one linear ditopic carboxylate has at least one phenyl group.

8. The method as defined in claim 7 wherein at least one functional group X is attached to the at least one phenyl group.

9. The method as defined in claim 5 wherein the crystallizing step is carried out by at least one of: leaving the solution at room temperature; adding a diluted base to the solution to initiate the crystallization; diffusing a diluted base into the solution to initiate the crystallization; and transferring the solution to a closed vessel and heating to a predetermined temperature.

10. The method as defined in claim 5 wherein the pore size and pore volume are systematically controlled.

11. The IRMOF as defined in claim 1 wherein the IRMOF has at least one of a predetermined pore size and functionality, and wherein the IRMOF is adapted to store at least one gas.

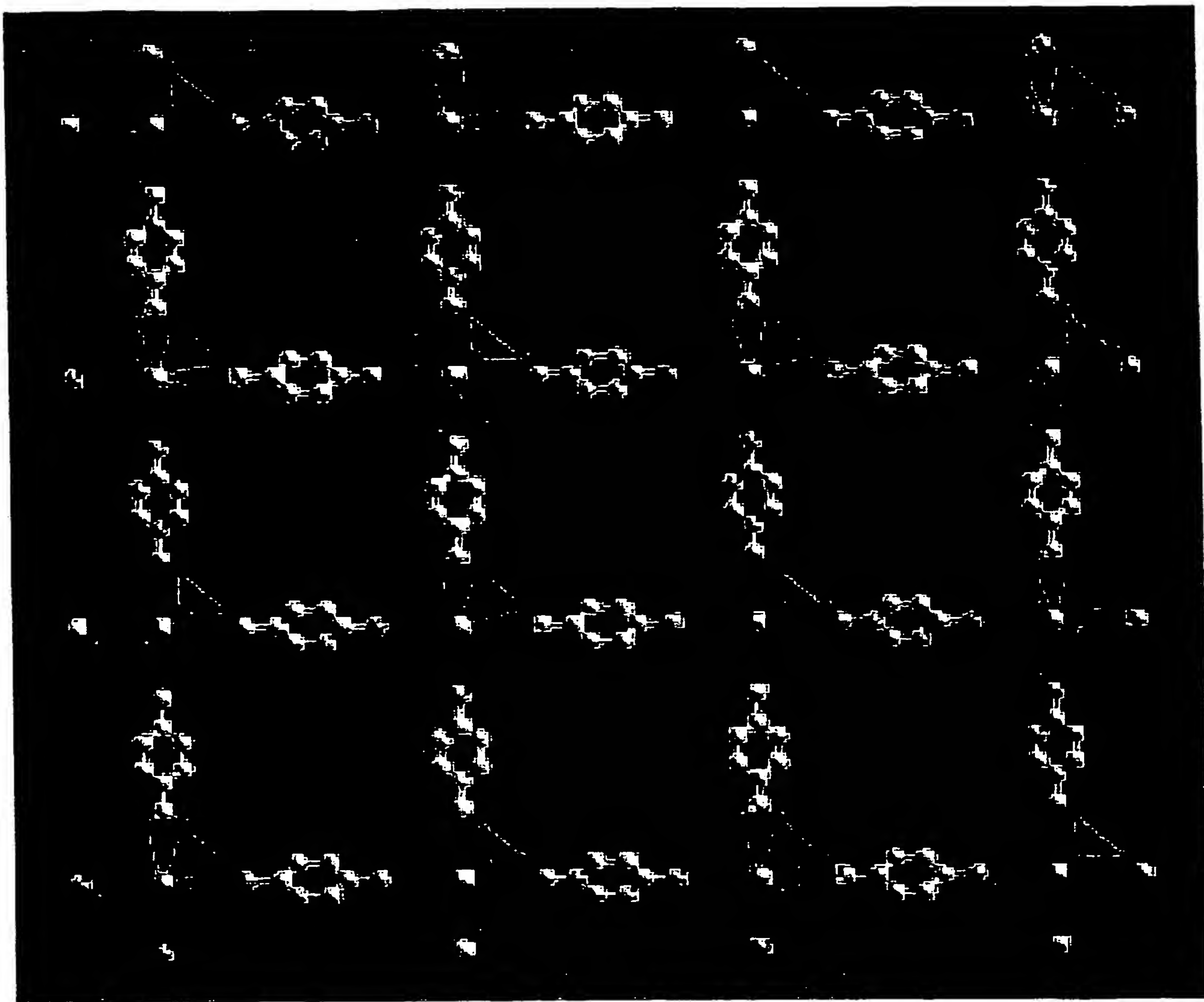
12. The IRMOF as defined in claim 11 wherein the at least one gas is methane.

13. The IRMOF as defined in claim 1 wherein the density of the IRMOF is between about 1.0 and about 0.2 g/cm<sup>3</sup>.

14. The IRMOF as defined in claim 13 wherein the density of the IRMOF is between about 0.41 and about 0.21 g/cm<sup>3</sup>.

15. The IRMOF as defined in claim 12, wherein the methane storage capacity is 155 cm<sup>3</sup>/cm<sup>3</sup>.

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**Figure 1**

XRPD of IRMOF-1 for Method 1

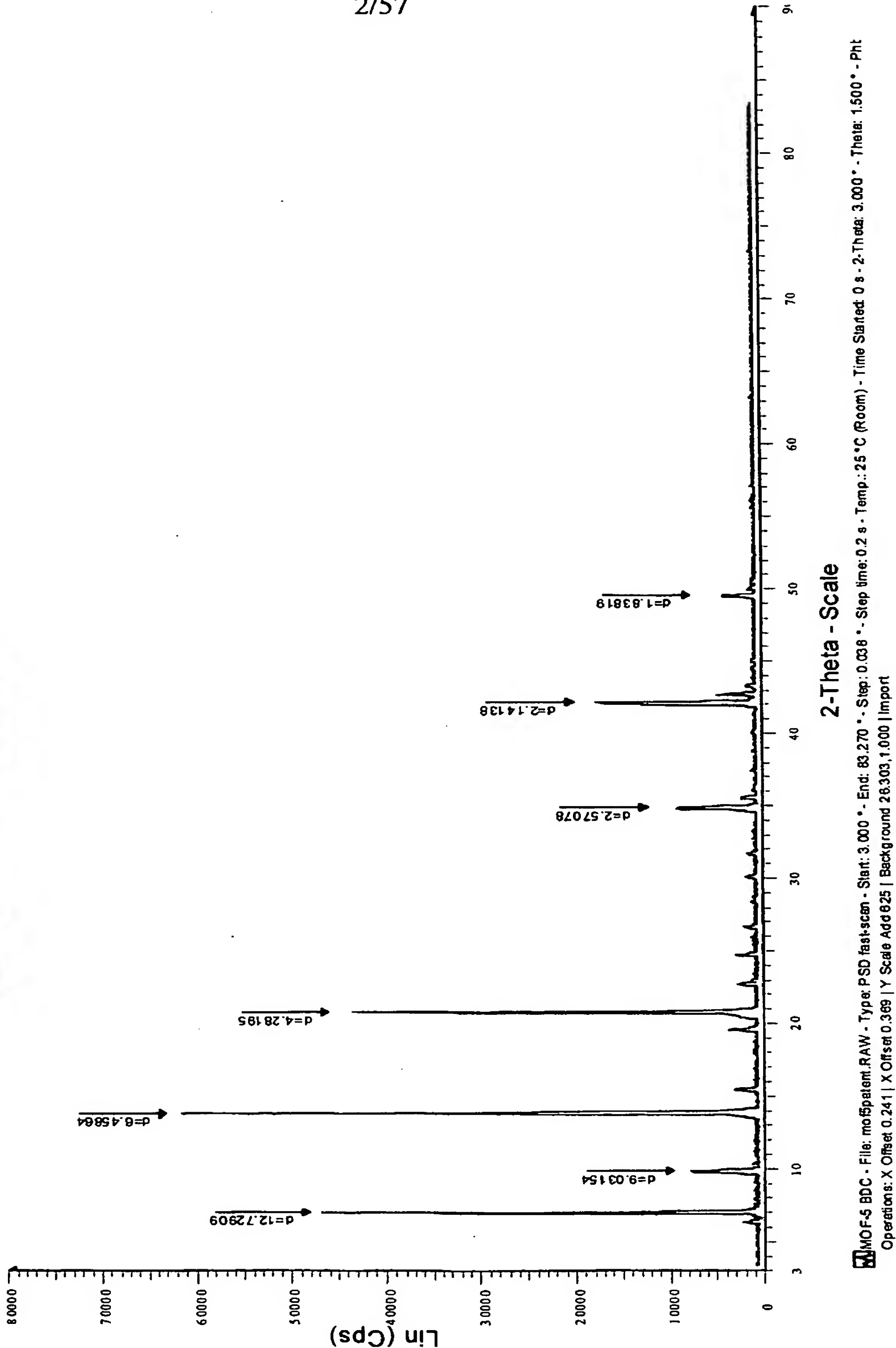


Figure 2a

XRPD of IRMOF-1 for Method 2

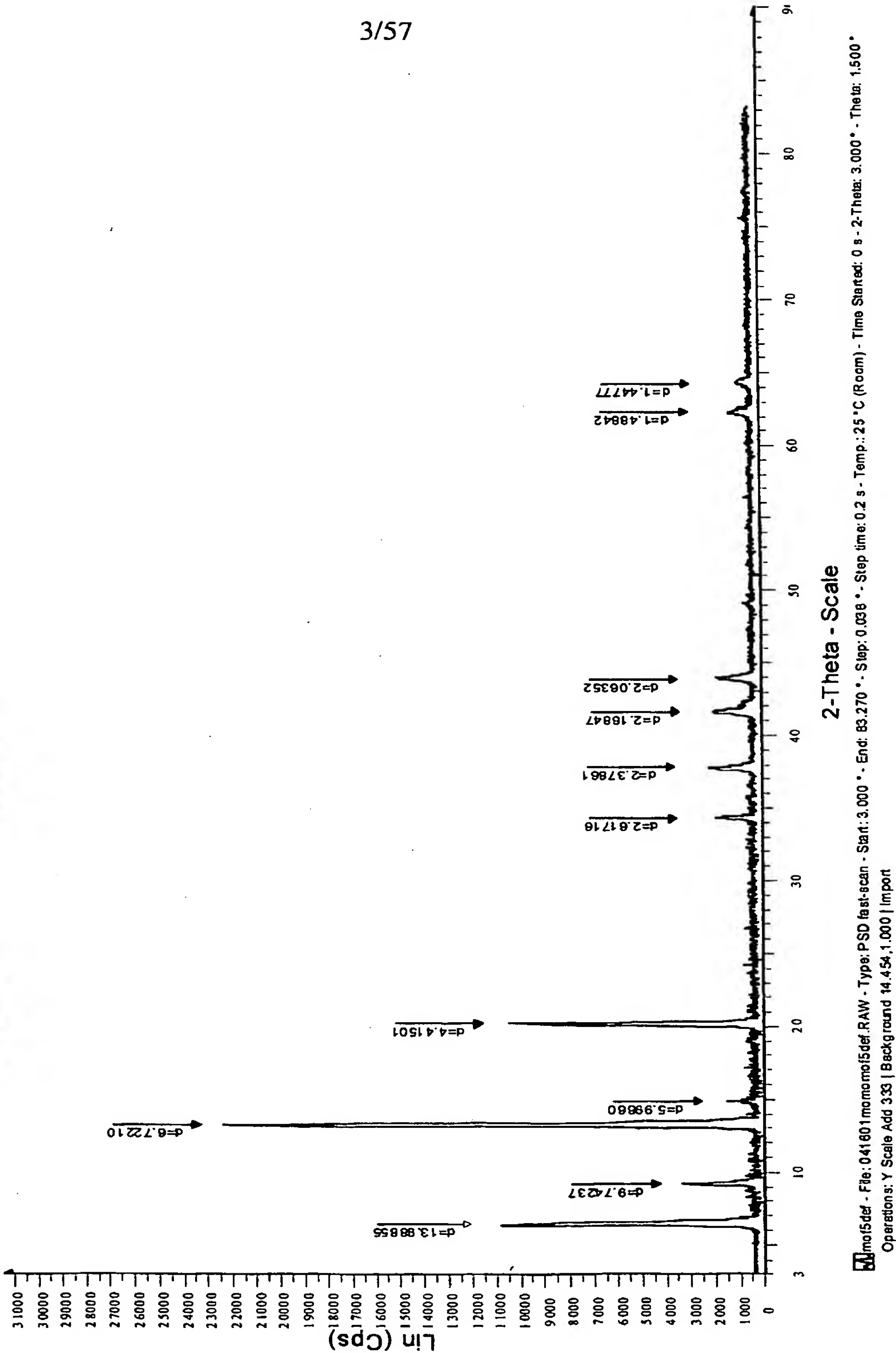
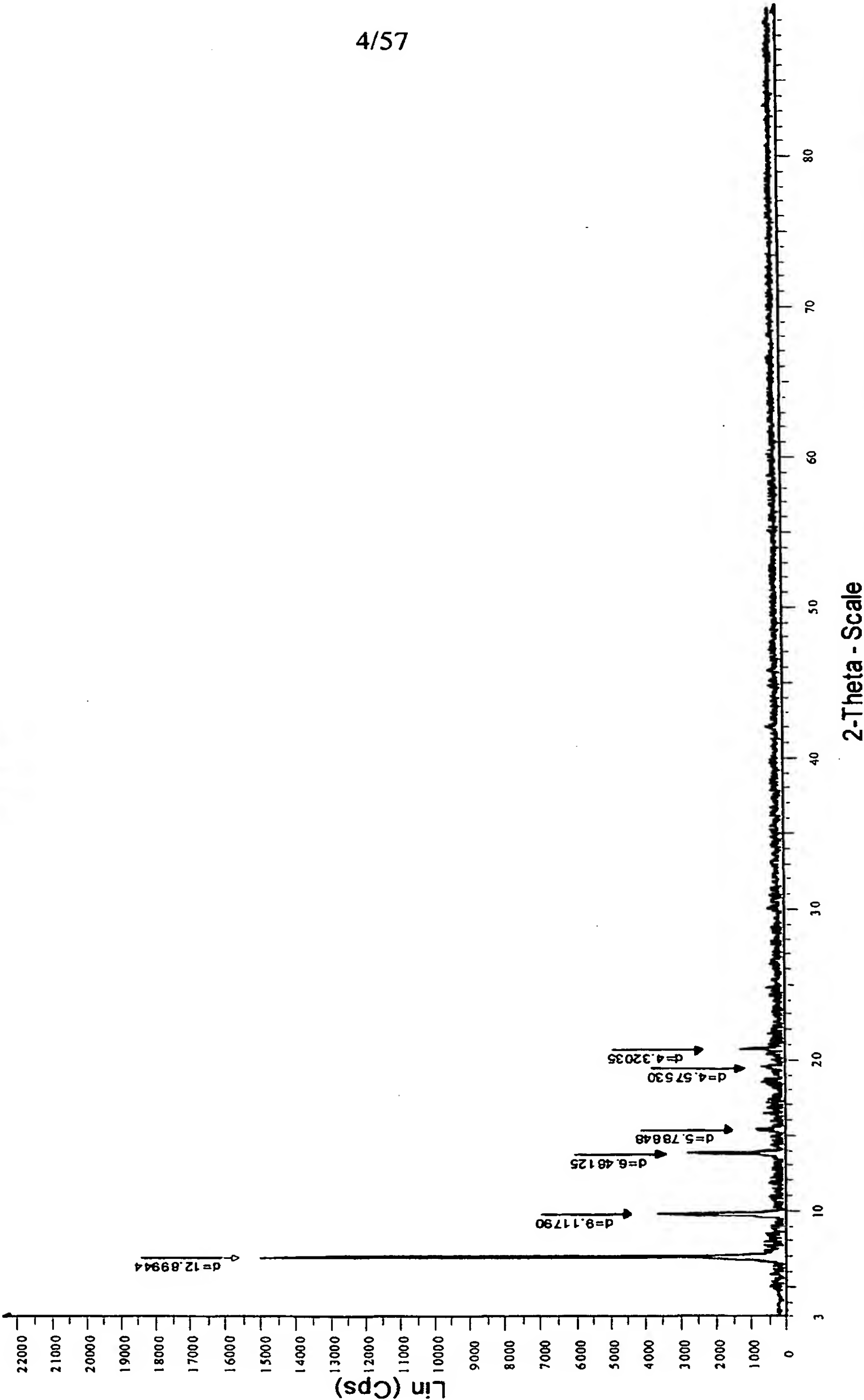


Figure 2b



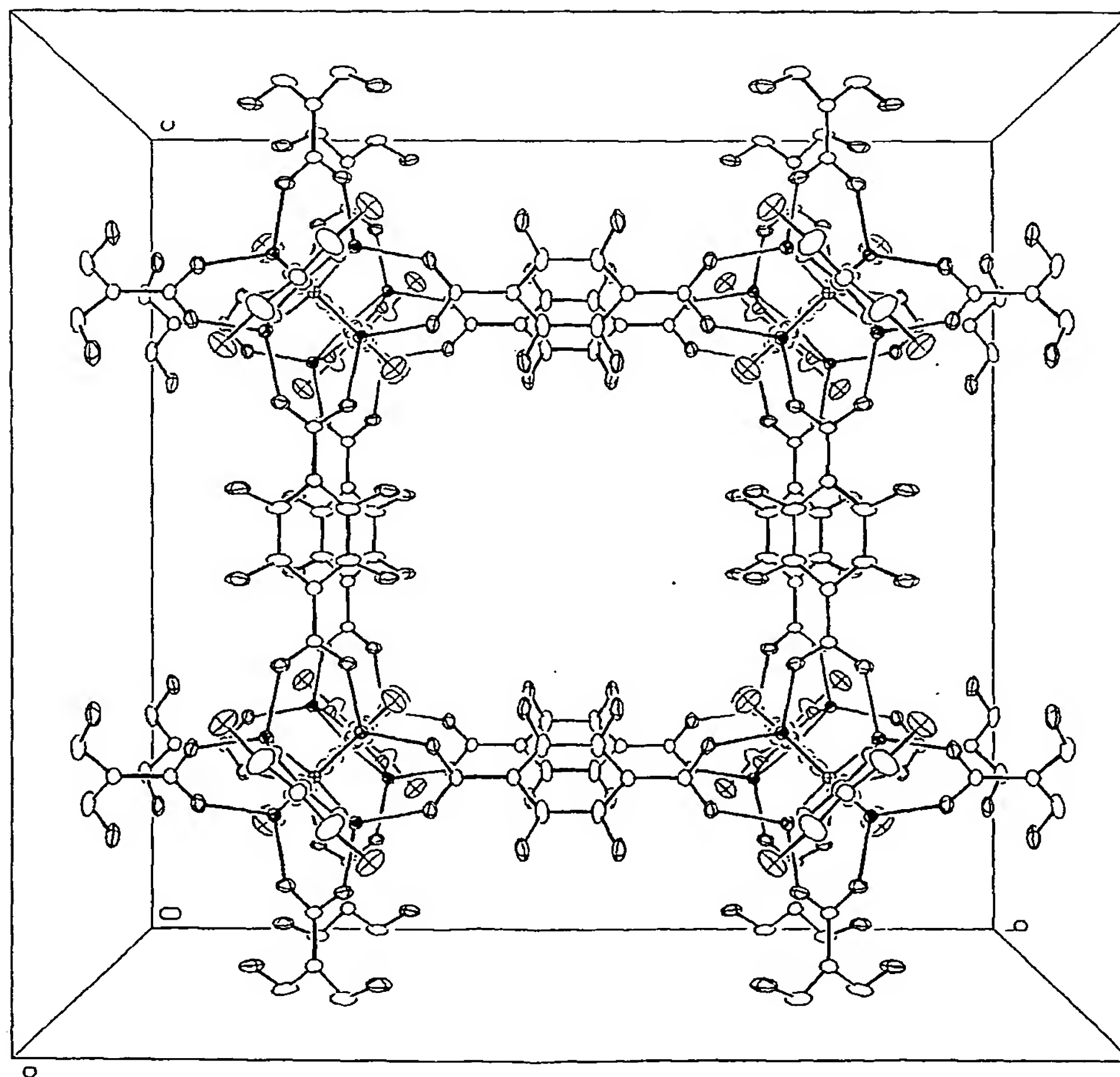
XRPD of IRMOF-1 for Method 3



File: momo53.RAW - Type: PSD fastscan - Start: 3.000 ° - End: 88.959 ° - Step: 0.042 ° - Step time: 0.2 s - Temp.: 25 °C (Room) - Time Started: 1 s - 2-Theta: 3.000 ° - Theta: 1.500 ° - Phi: 0.00 ° - A  
Operations: Y Scale Add 167 | Background 8,128,1,000 | Import

Figure 2c

# Crystal Structure for IRMOF-3

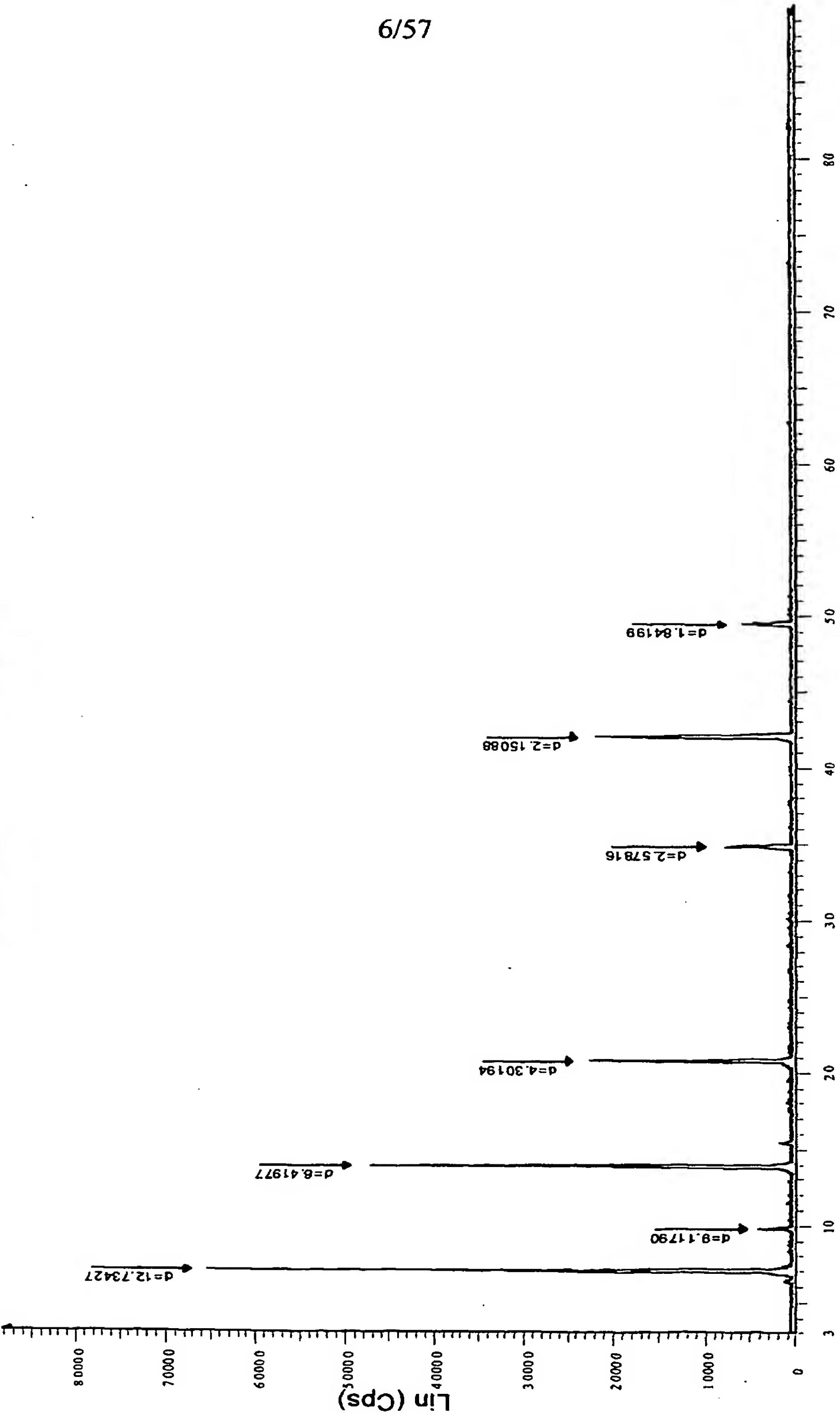


Crystal data  
Cubic, *Fm-3m*  
*a* = 25.7465(14) Å  
*V* = 17066.9(16) Å<sup>3</sup>  
*R*1 = 0.1201 [*I* > 2σ(*I*)]  
*wR*2 = 0.3437 (all data)

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Figure 3

XRPD of IRMOF-3

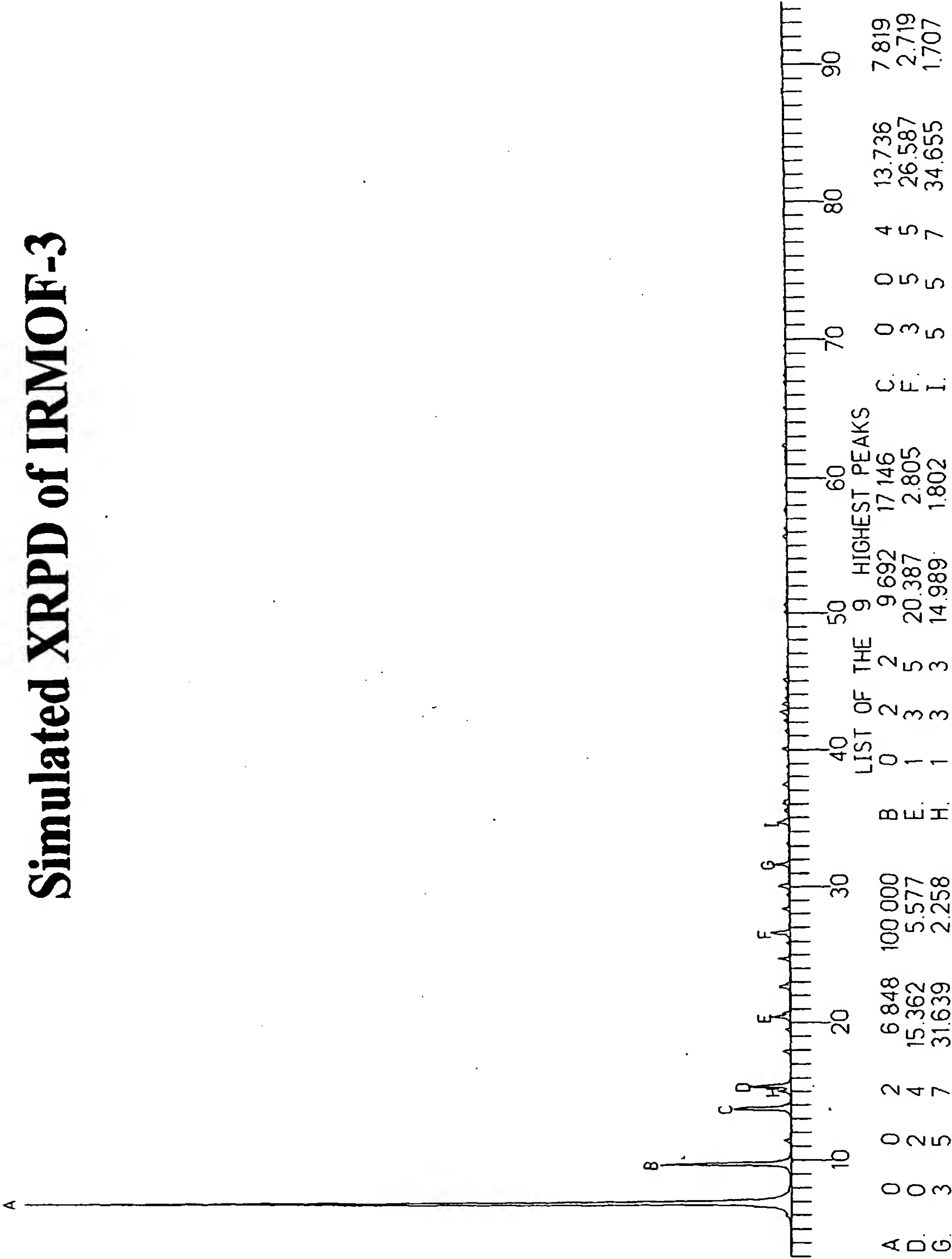


2-Theta - Scale

File: monoaminoBDCDEF.RAW - Type: PSD fast-scan - Start: 3.000 ° - End: 89.959 ° - Step: 0.042 ° - Step time: 0.2 s - Temp.: 25 °C (Room) - Time Started: 1 s - 2-Theta: 3.000 ° - Theta: 1.500  
Operations: Y Scale Add 333 | Background 26.303,1.000 | Import

Figure 4a

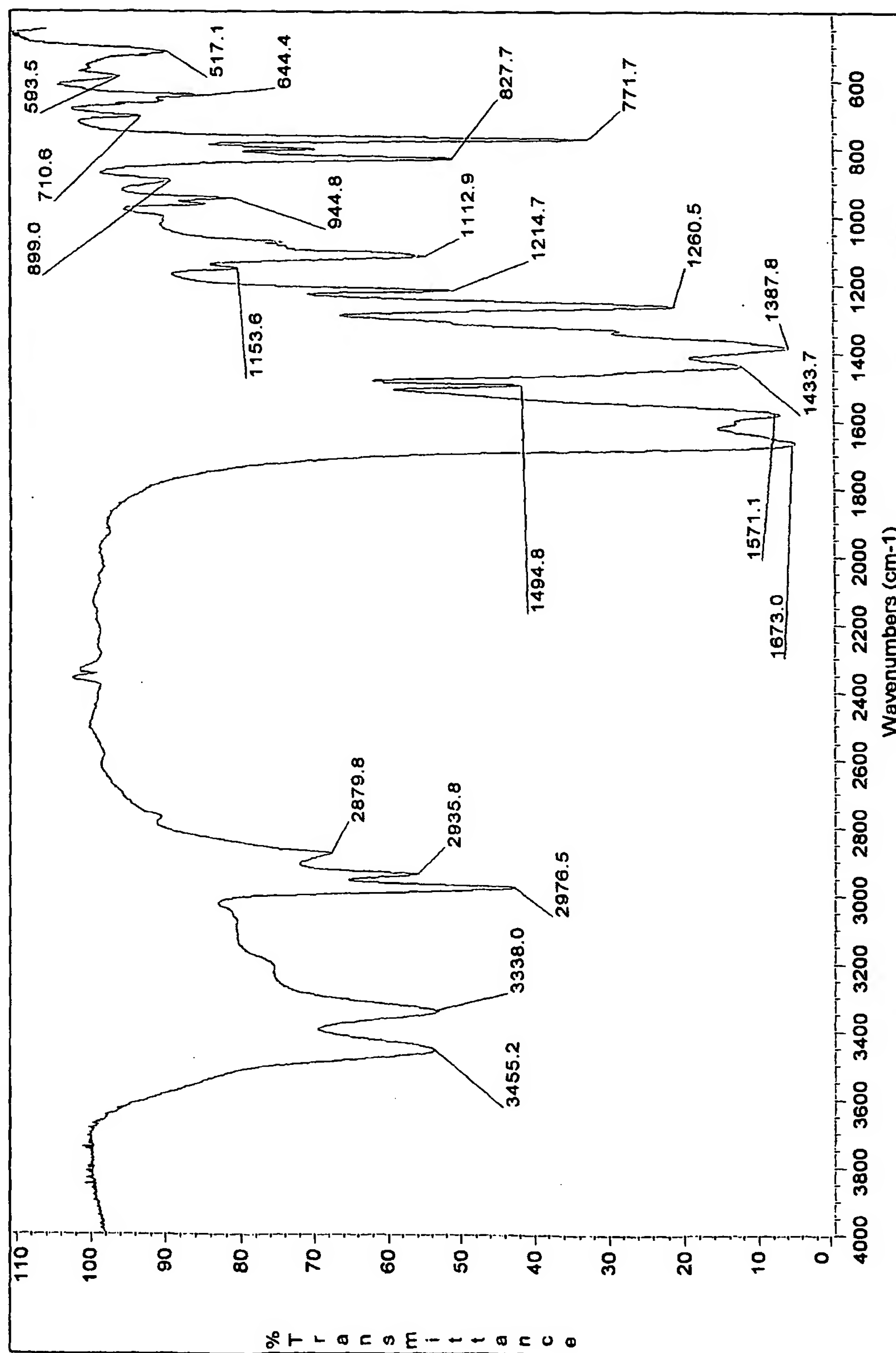
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**Figure 4b**

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# InfraRed spectrum for IRMOF-3

**Figure 5**



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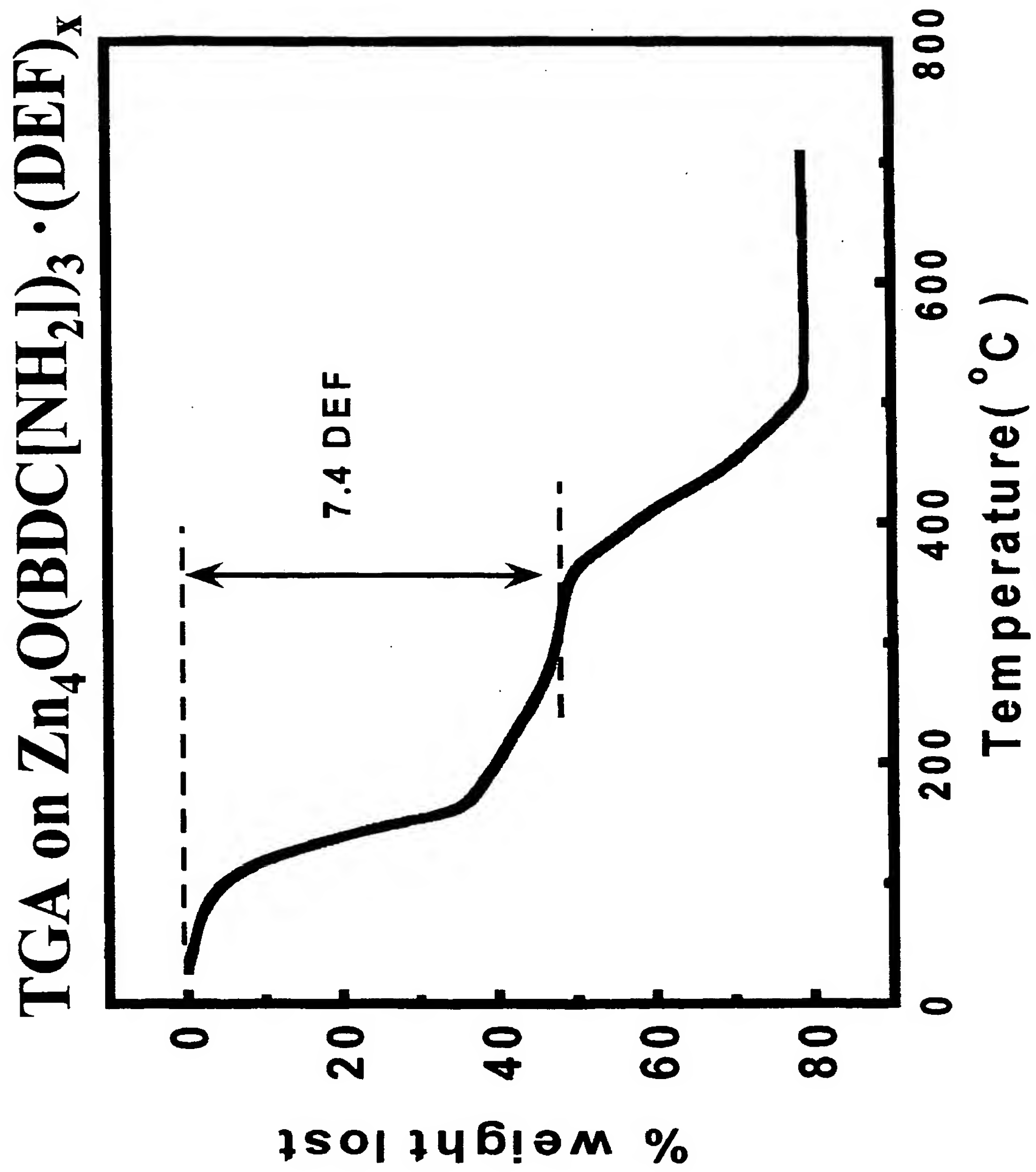


Figure 6

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Infra-Red spectrum for  $\text{Zn}_4\text{O}(\text{BDC}[\text{NH}_2])_3 \cdot (\text{CHCl}_3)_x$

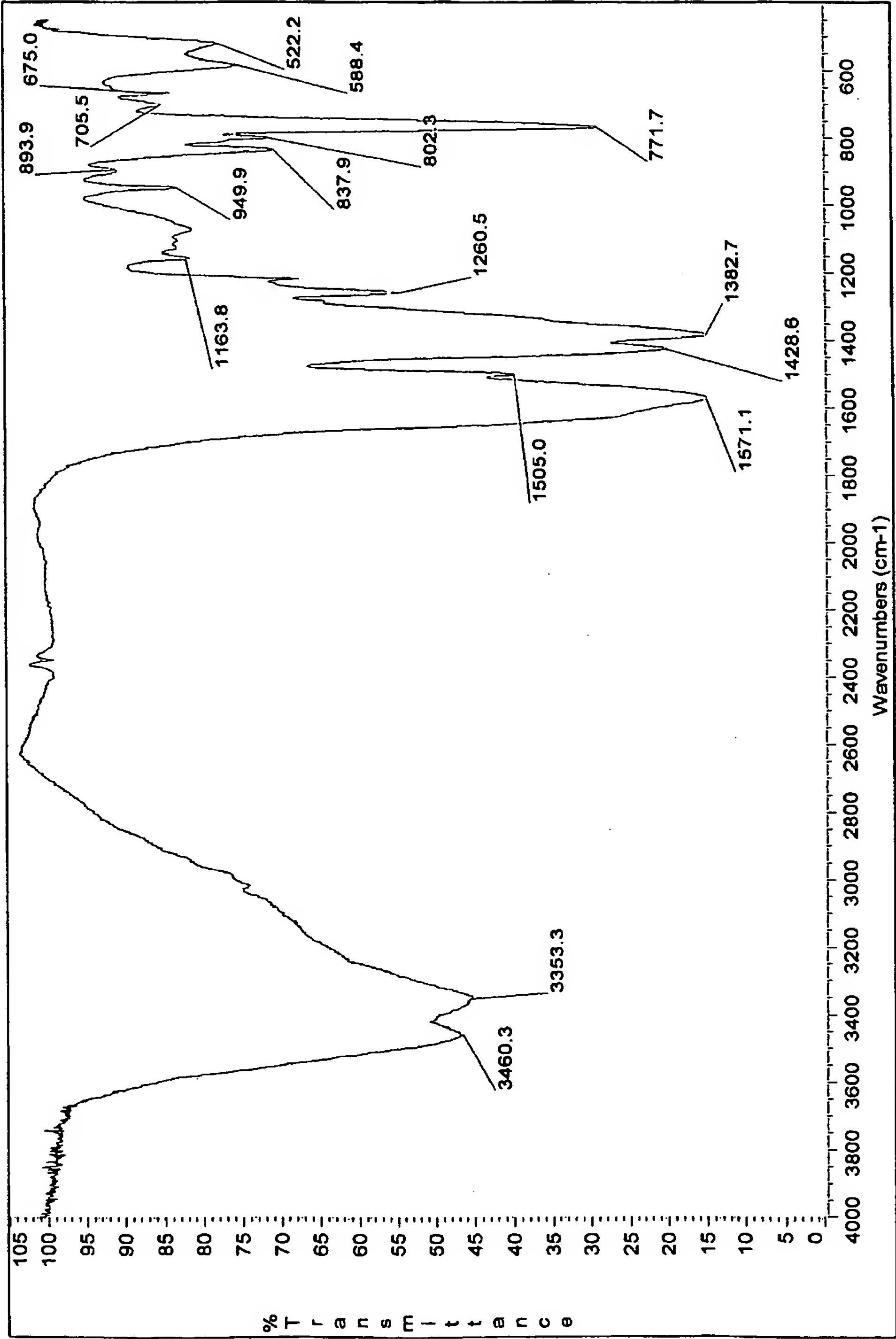


Figure 7

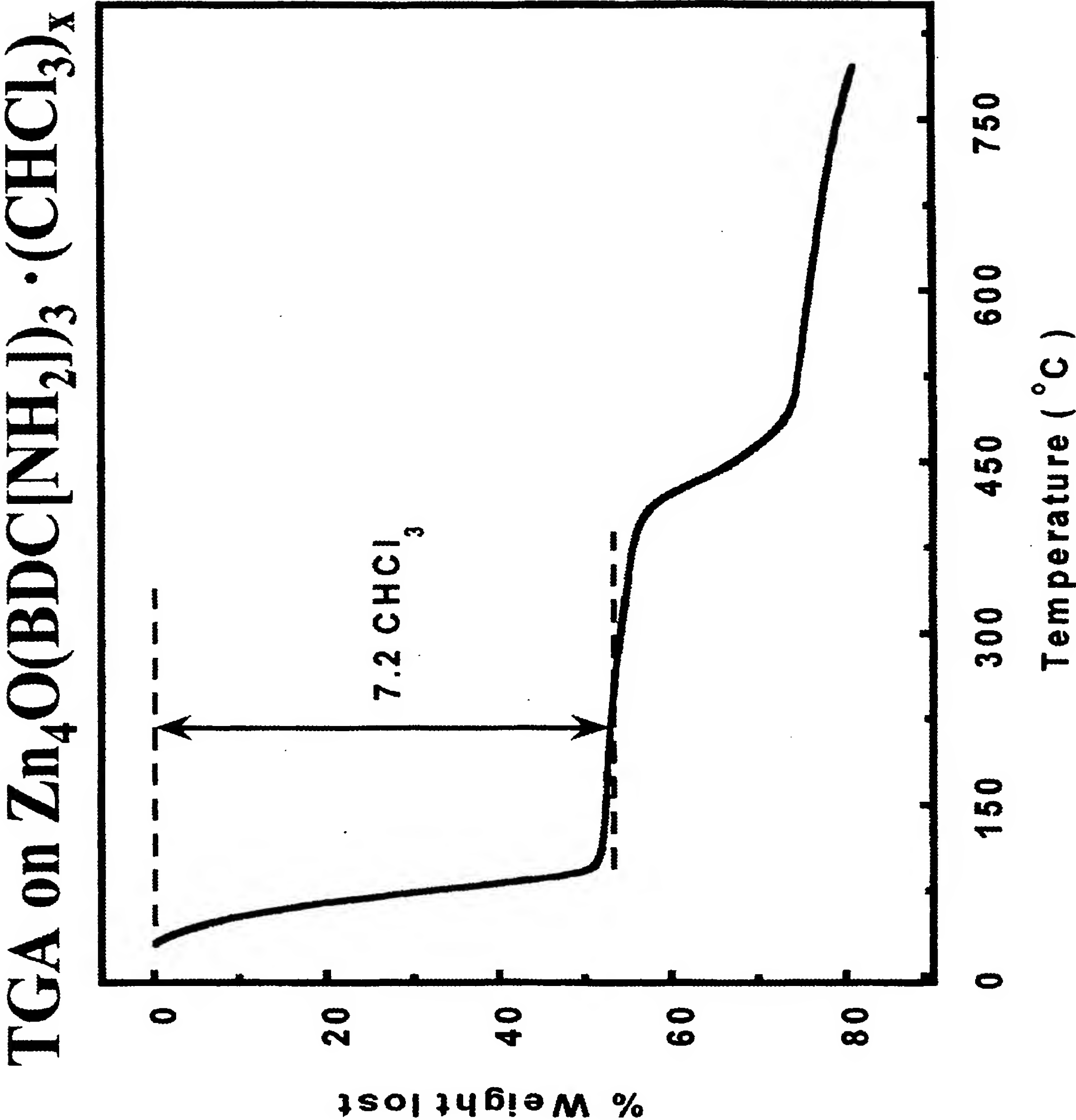


Figure 8

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N<sub>2</sub> Sorption on IRMOF-3 @ 77K

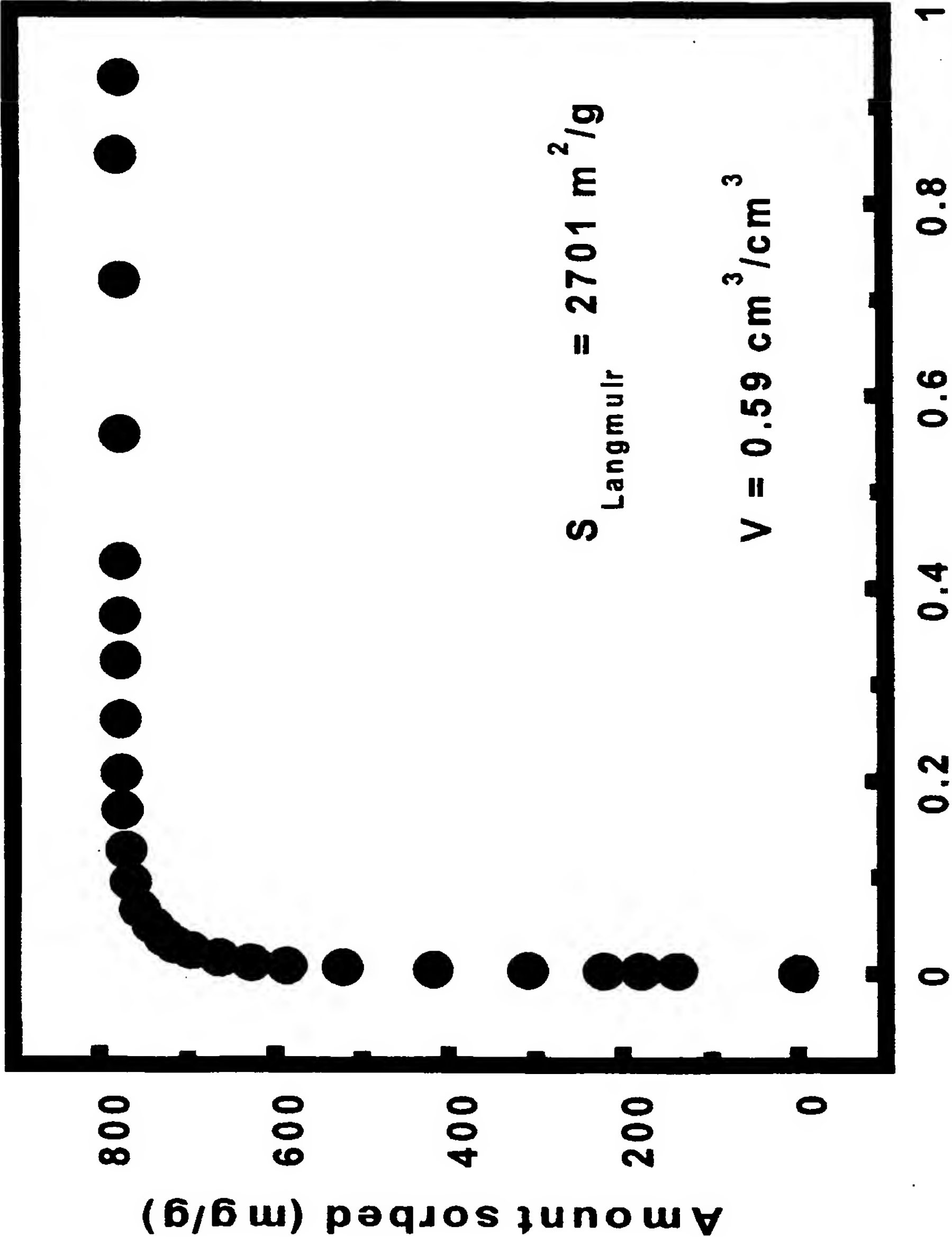


Figure 9

Organic vapor sorption at RT on IRMOF-3

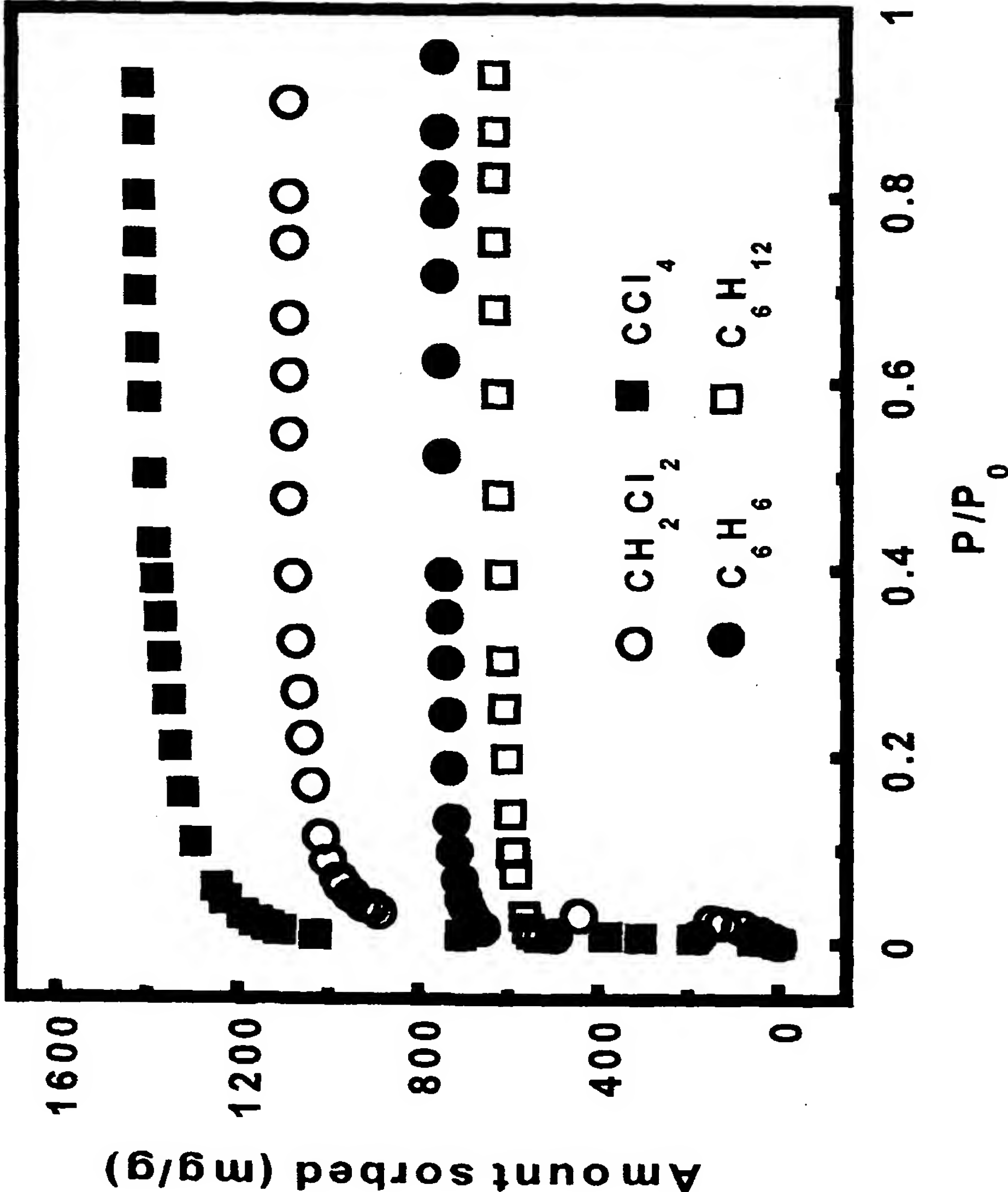
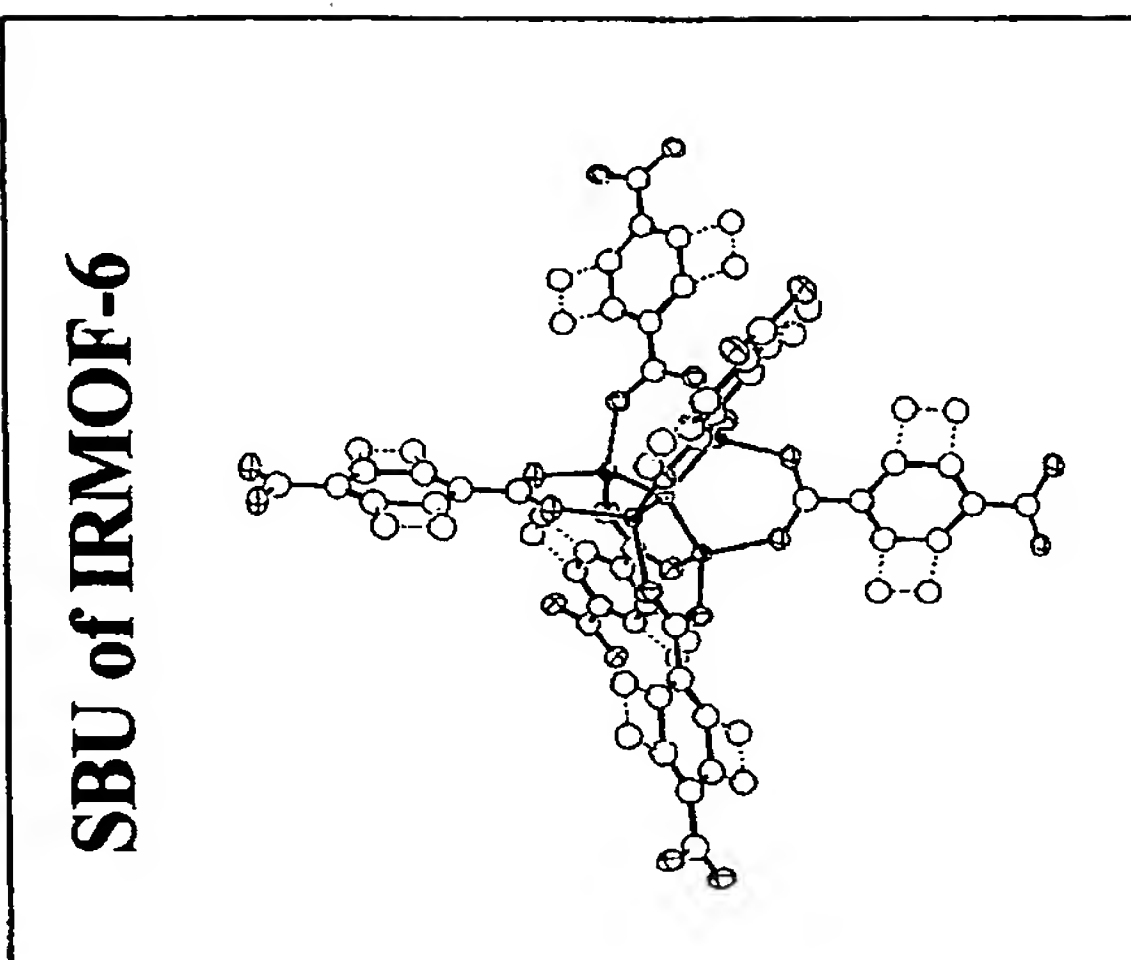
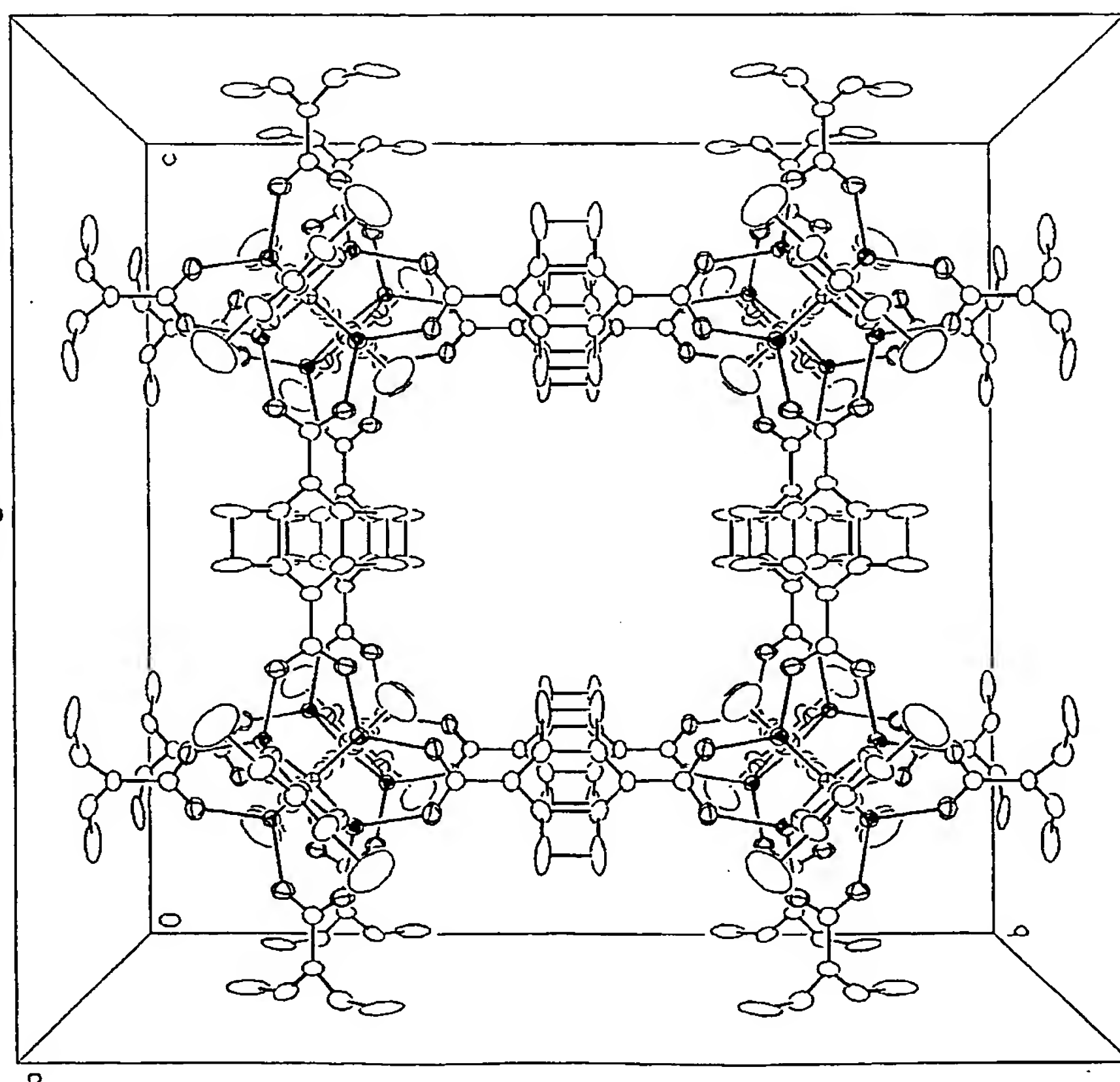


Figure 10

# Crystal Structure for IRMOF-6



## Crystal data

Cubic,  $Fm-3m$

$a = 25.8421(15) \text{ \AA}$

$V = 17257.7(17) \text{ \AA}^3$

$R1 = 0.1366 [I > 2\sigma(I)]$

$wR2 = 0.5067$  (all data)

Figure 11



XRPD of IRMOF-6

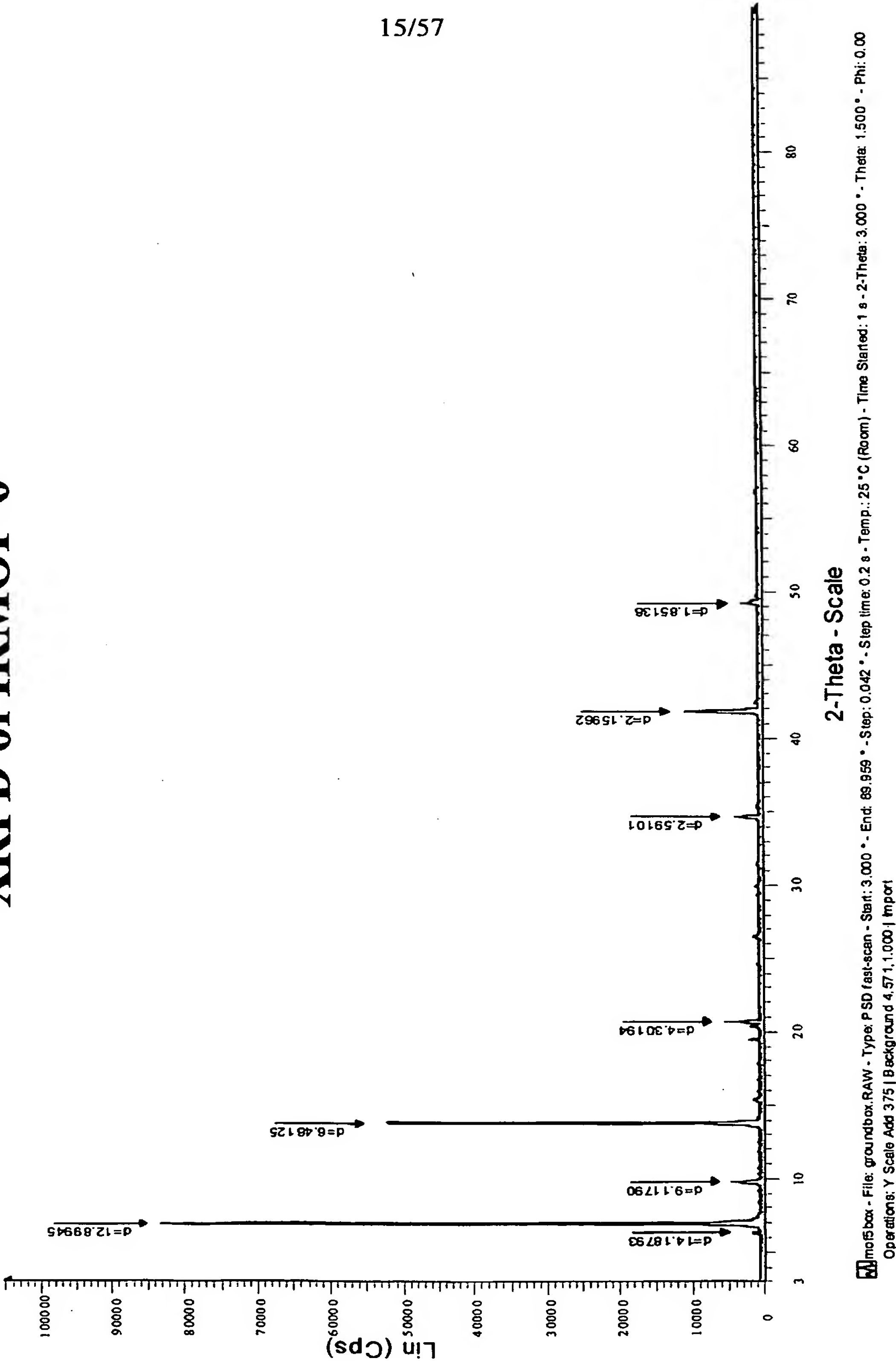


Figure 12a

Simulated XRPD of IRMOF-6

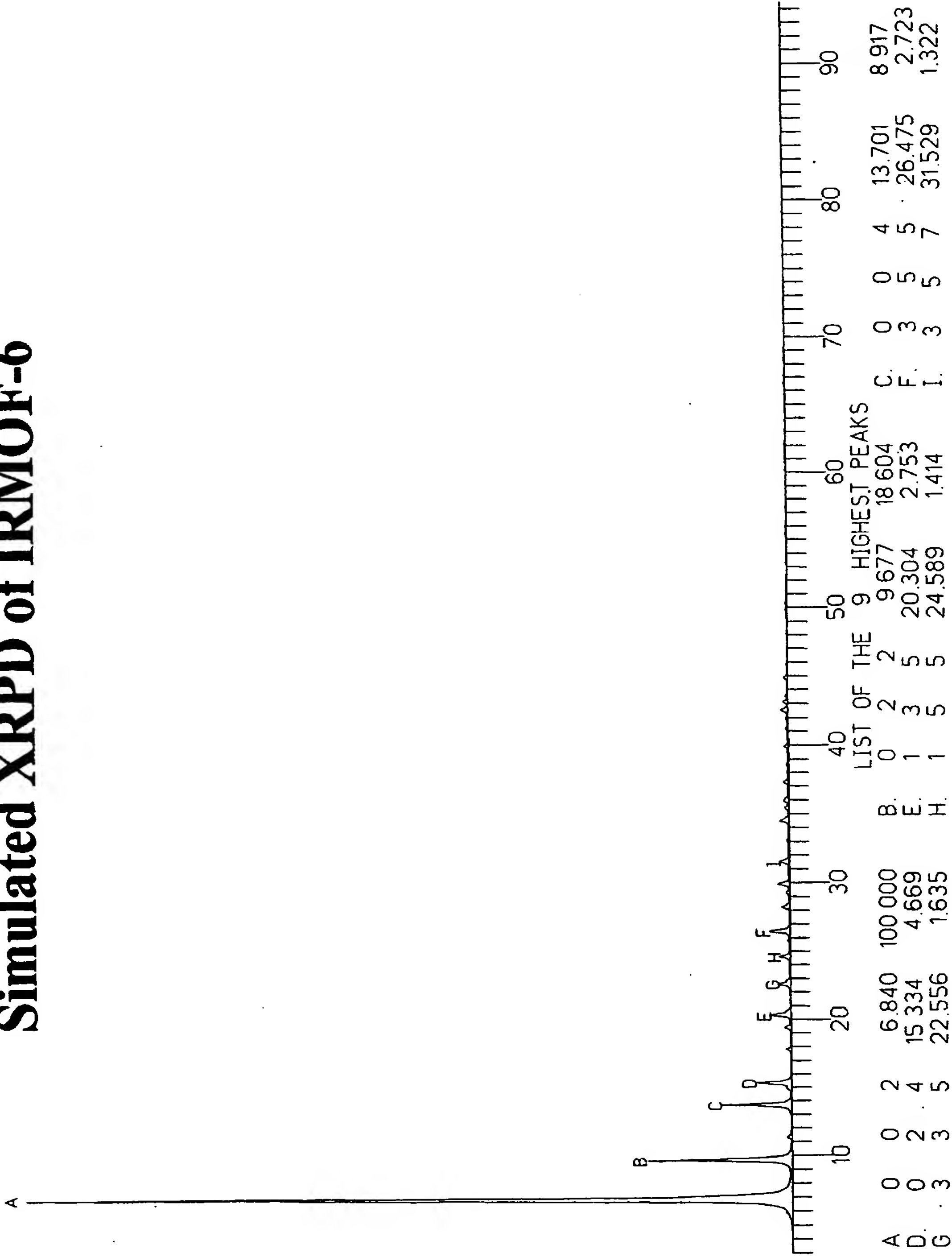


Figure 12b

# InfraRed spectrum for IRMOF-6

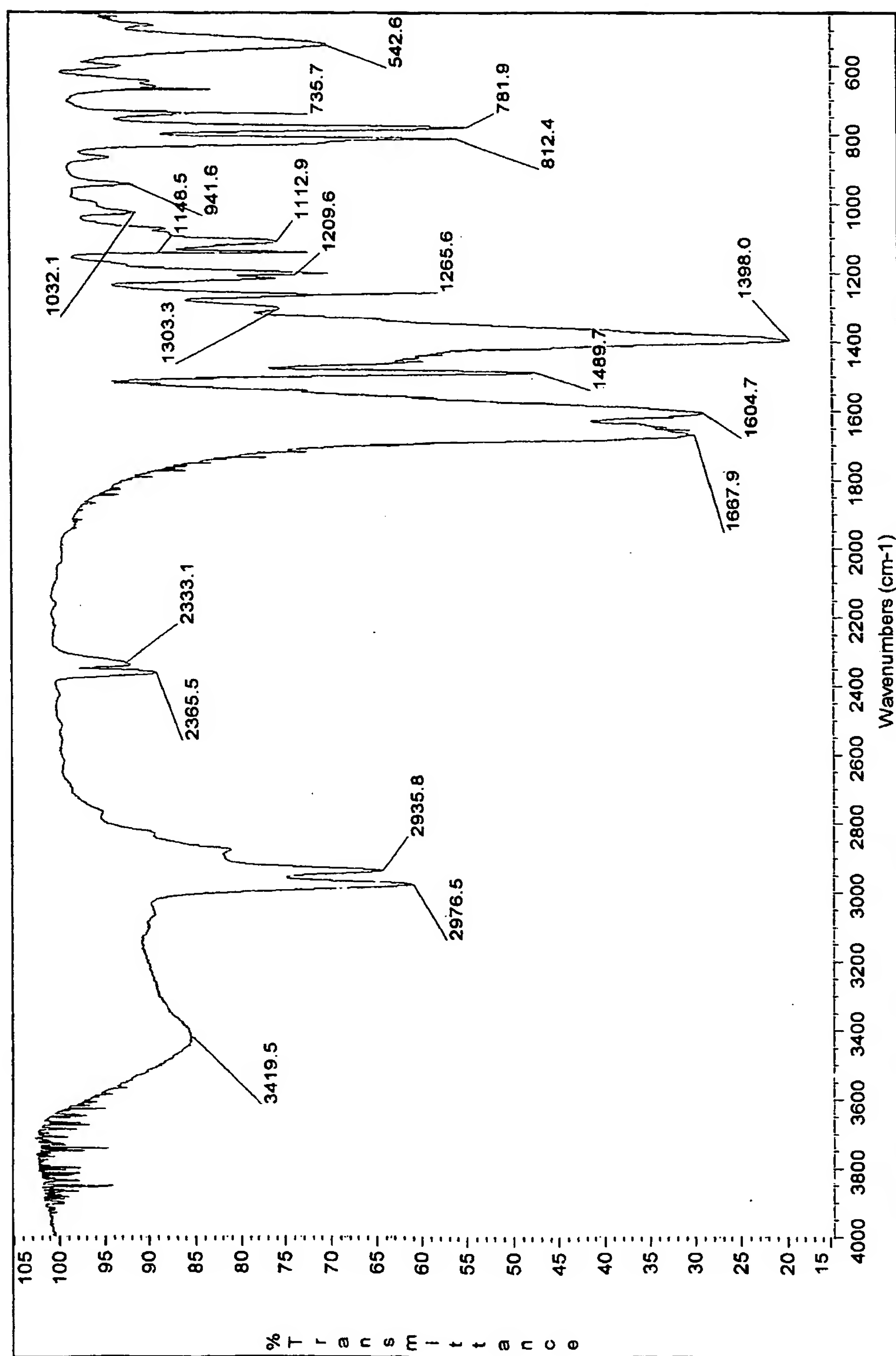


Figure 13

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TGA for IRMOF-6,  $\text{Zn}_4\text{O}(\text{BDC}[\text{C}_2\text{H}_4])_3 \cdot (\text{DEF})_x$

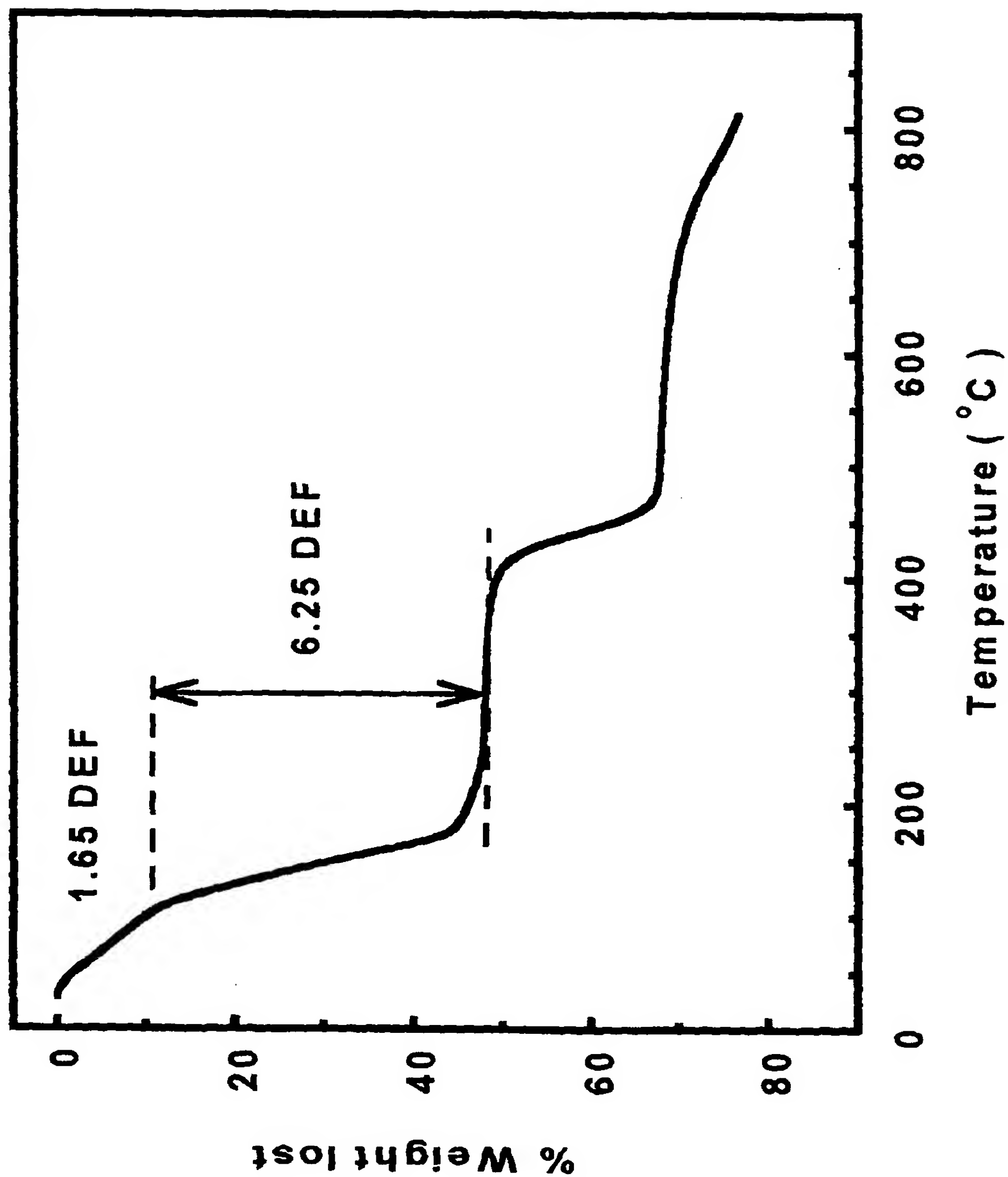


Figure 14

# InfraRed spectrum for $\text{Zn}_4\text{O}(\text{BDC}[\text{C}_2\text{H}_4]_3 \cdot (\text{CHCl}_3)_x$

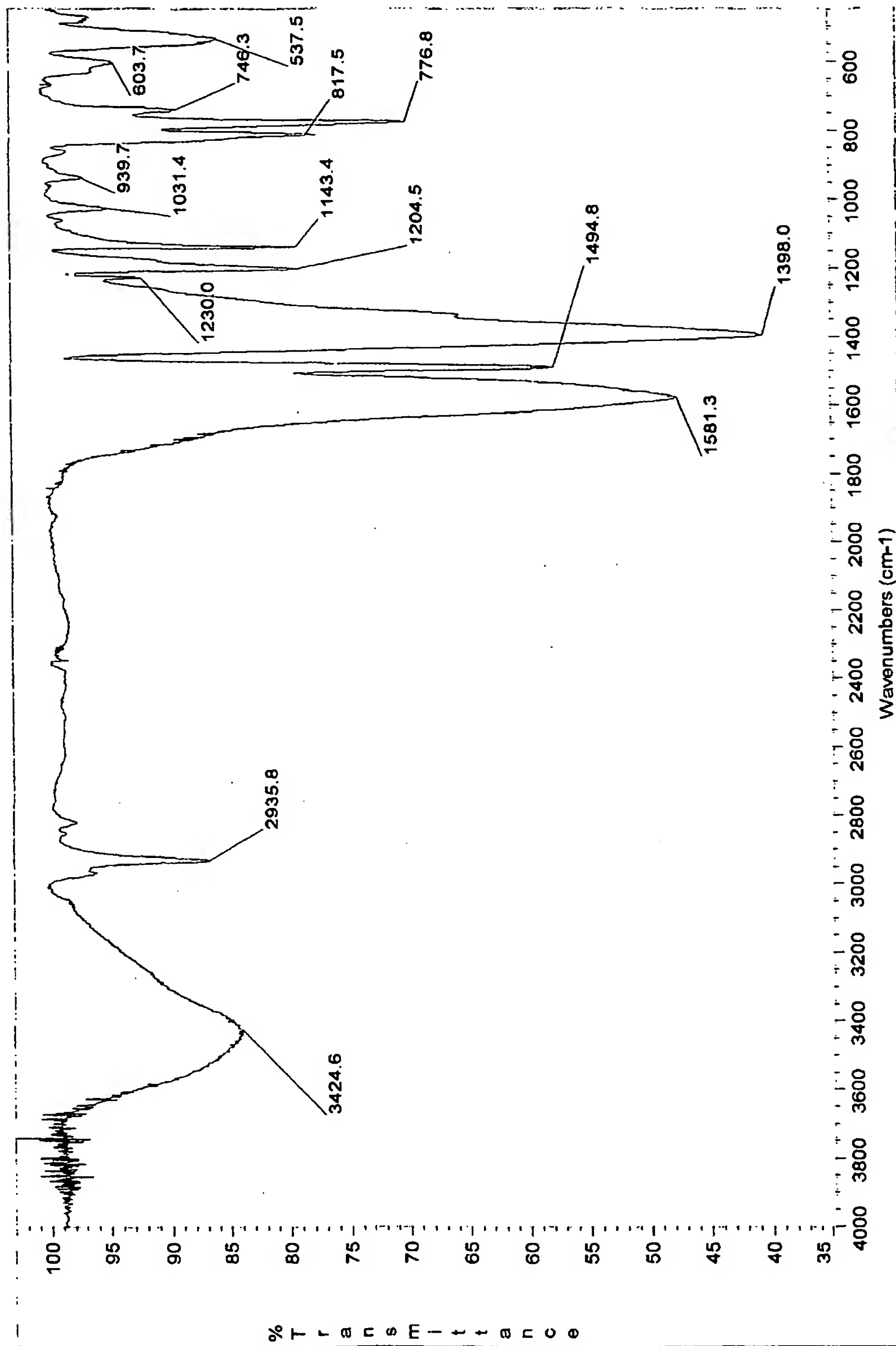


Figure 15

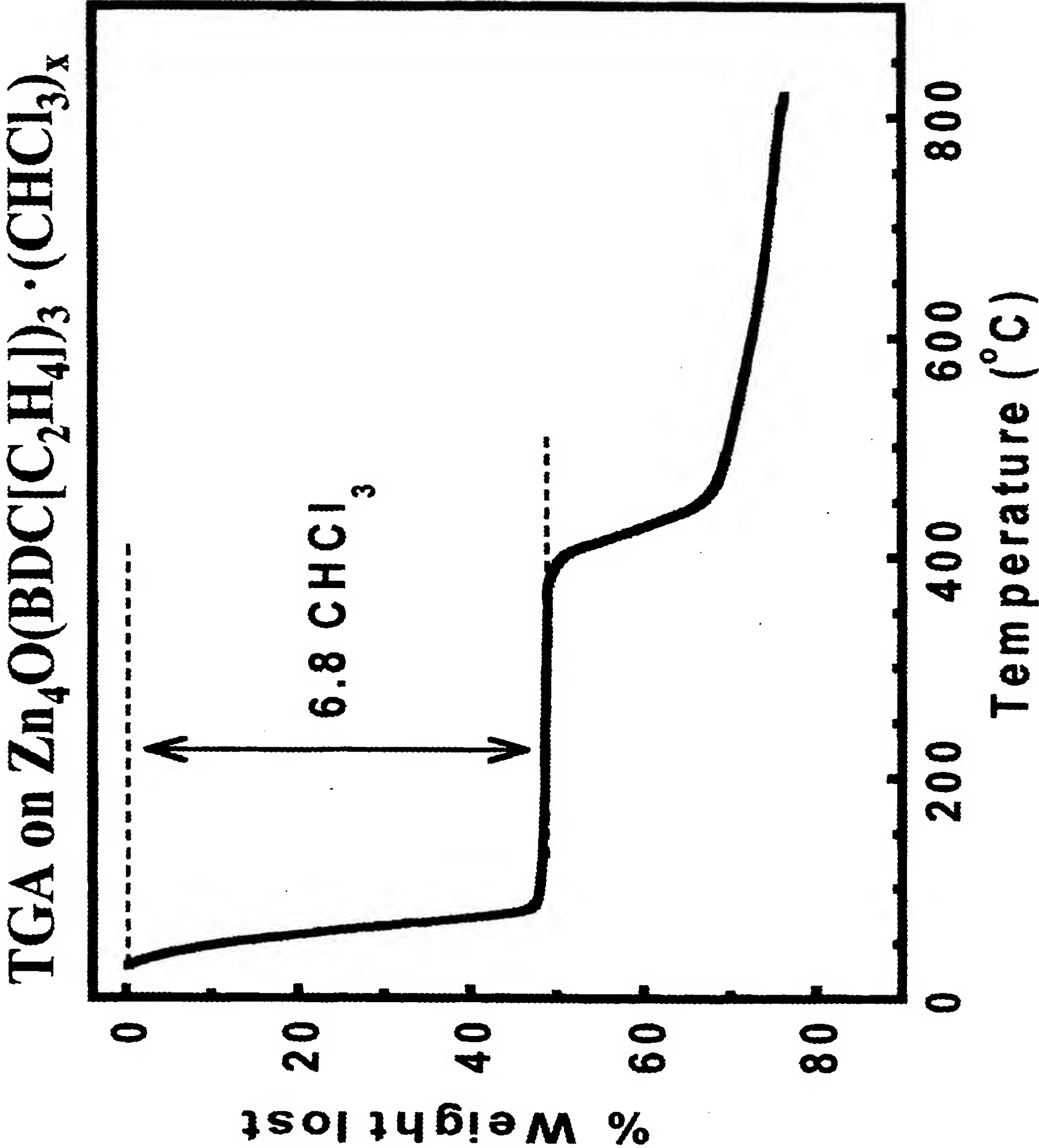
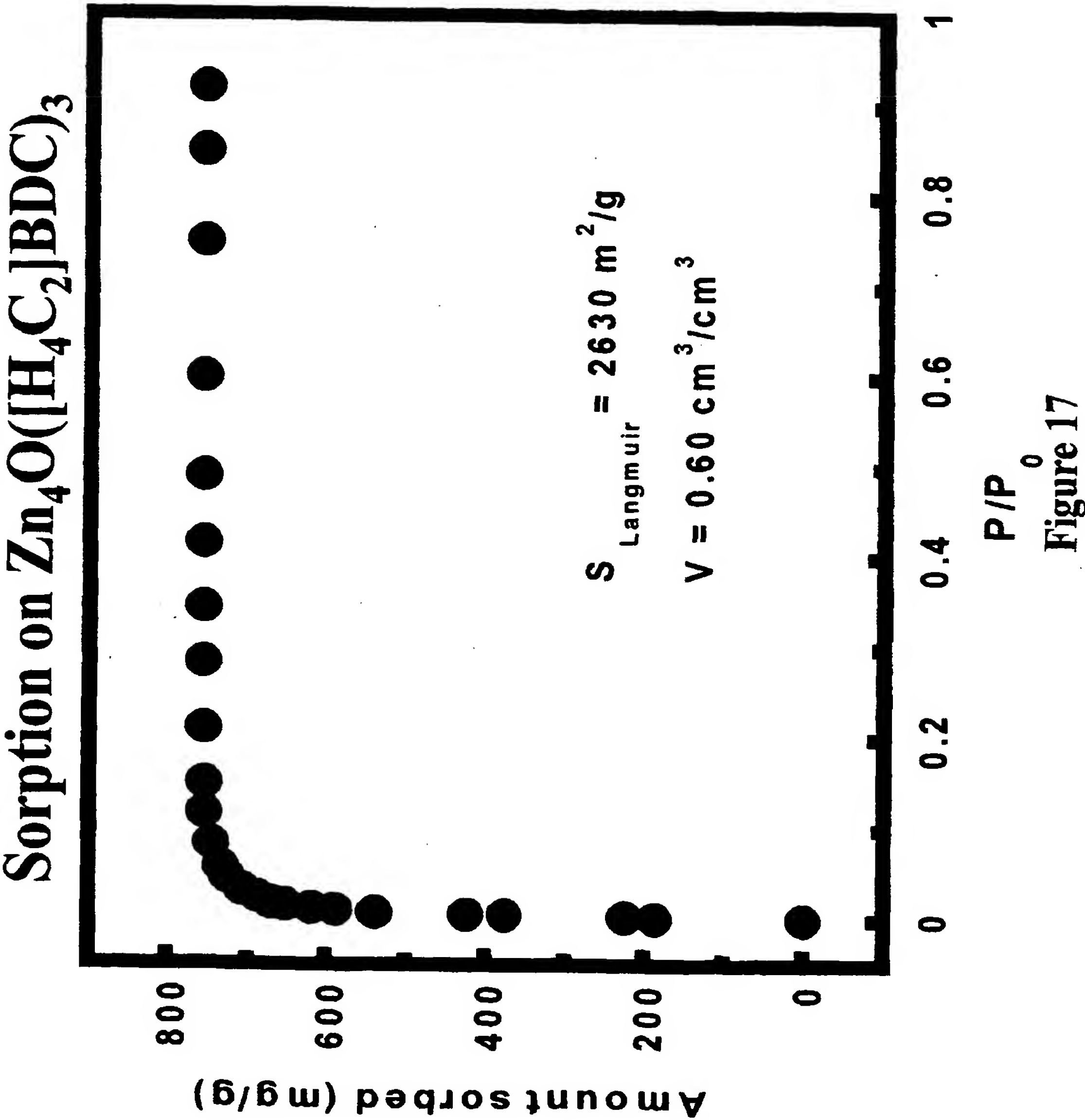
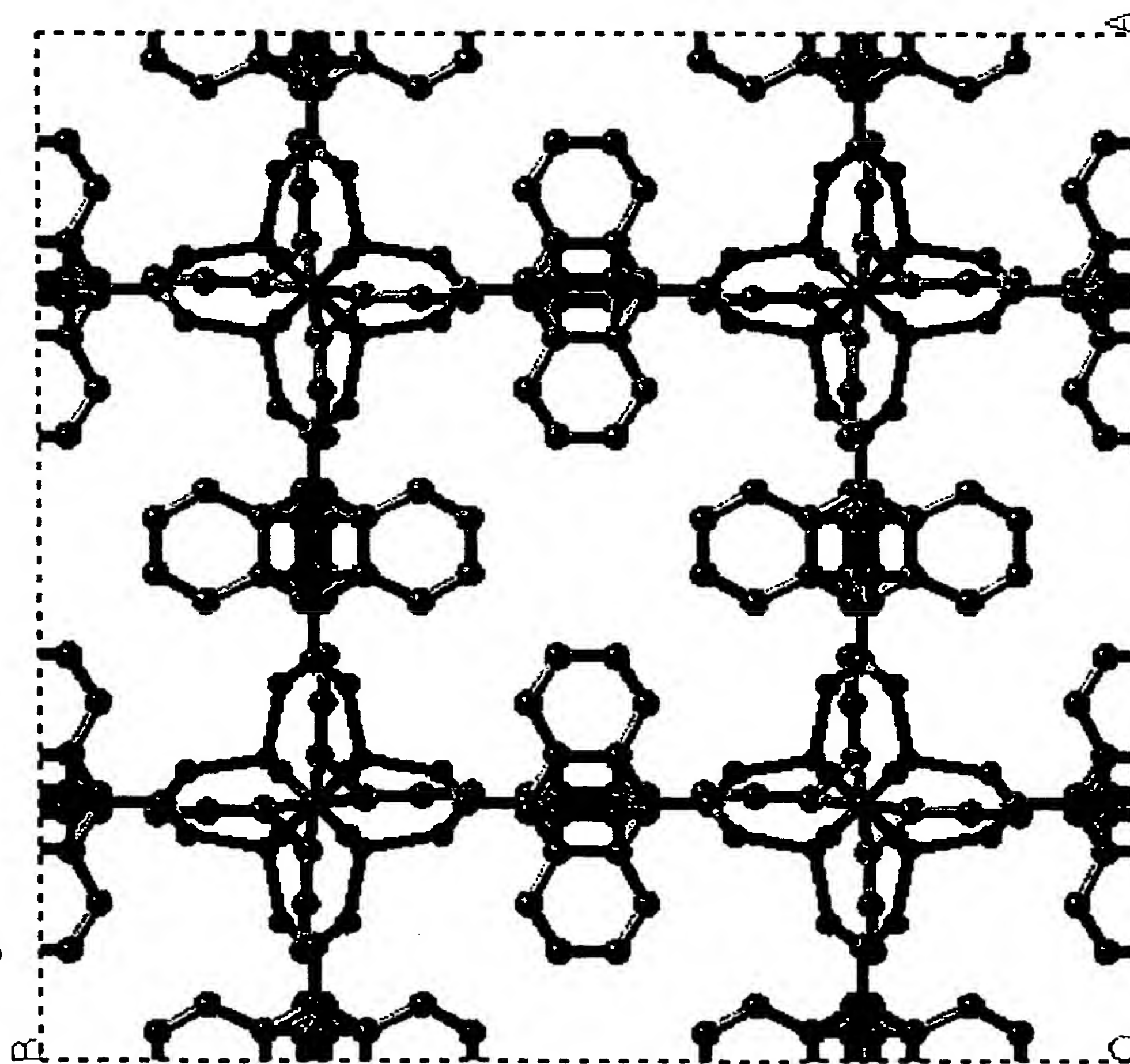


Figure 16





# Crystal Structure for IRMOF-7



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Crystal data  
Cubic,  $Pm-3m$   
 $a = 12.914(3) \text{ \AA}$   
 $V = 2153.9 \text{ \AA}^3$

Figure 18

# XRPD of IRMOF-7

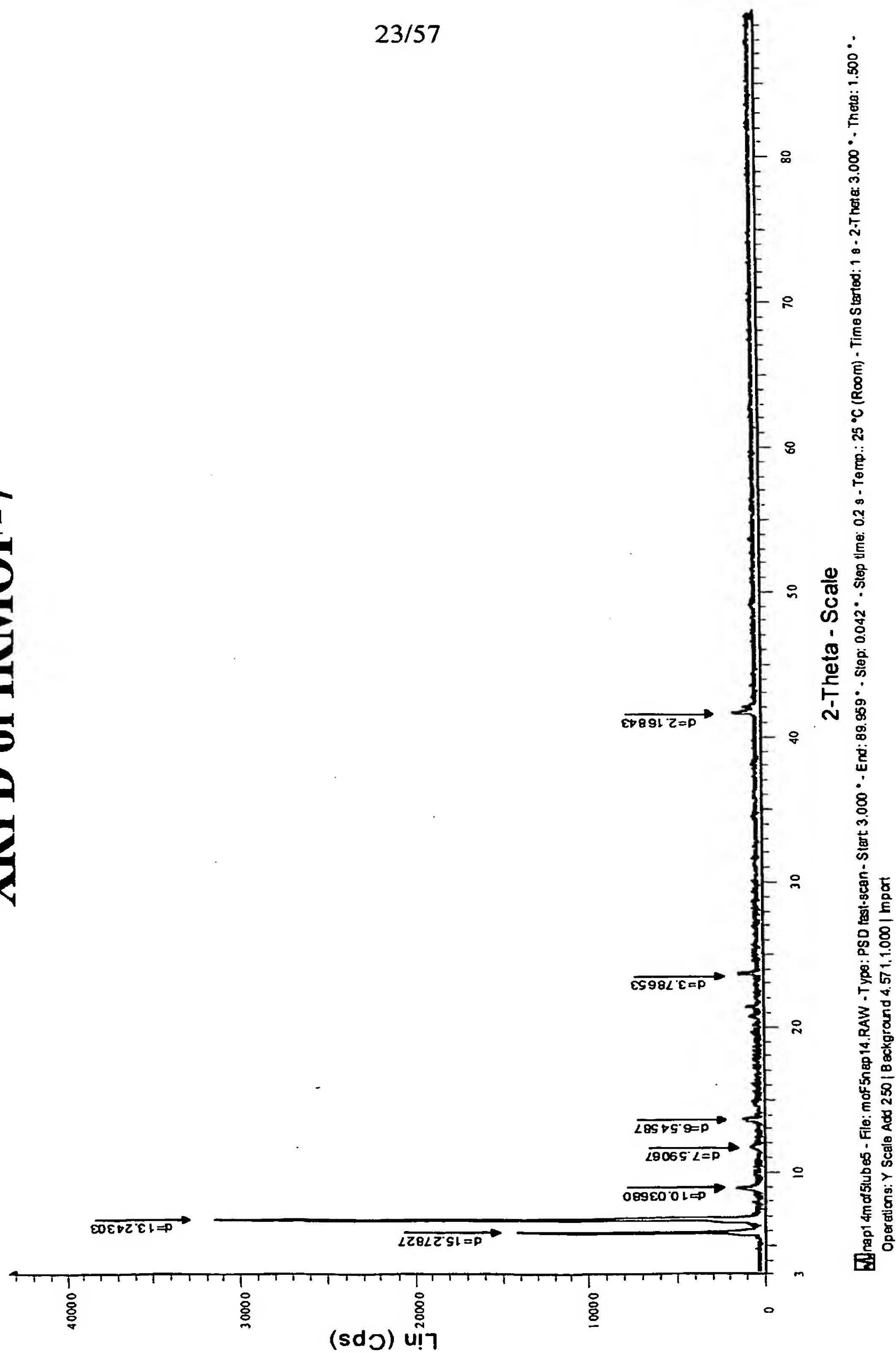


Figure 19a

Simulated XRPD of IRMOF-7

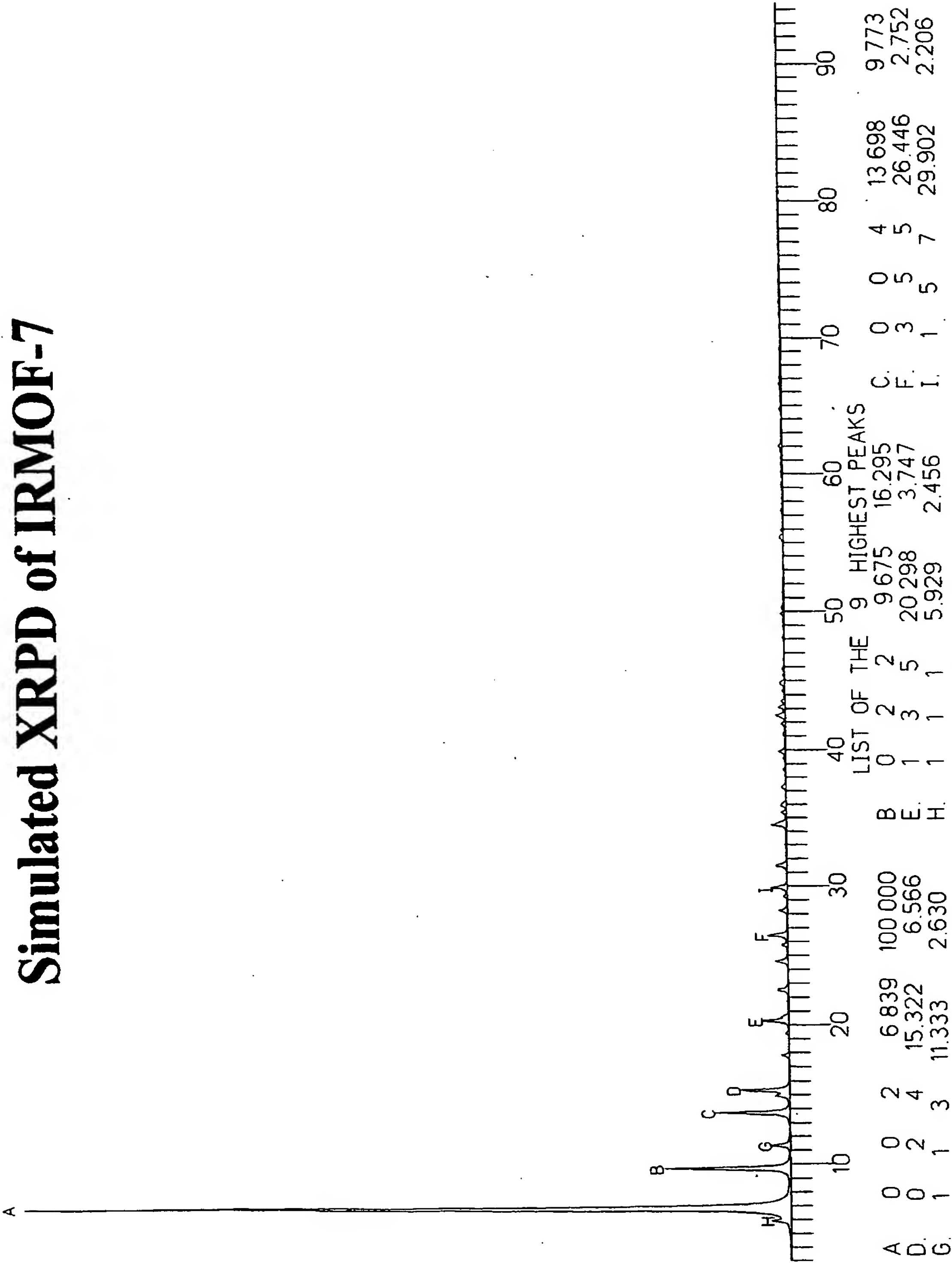


Figure 19b

XRPD of IRMOF-8

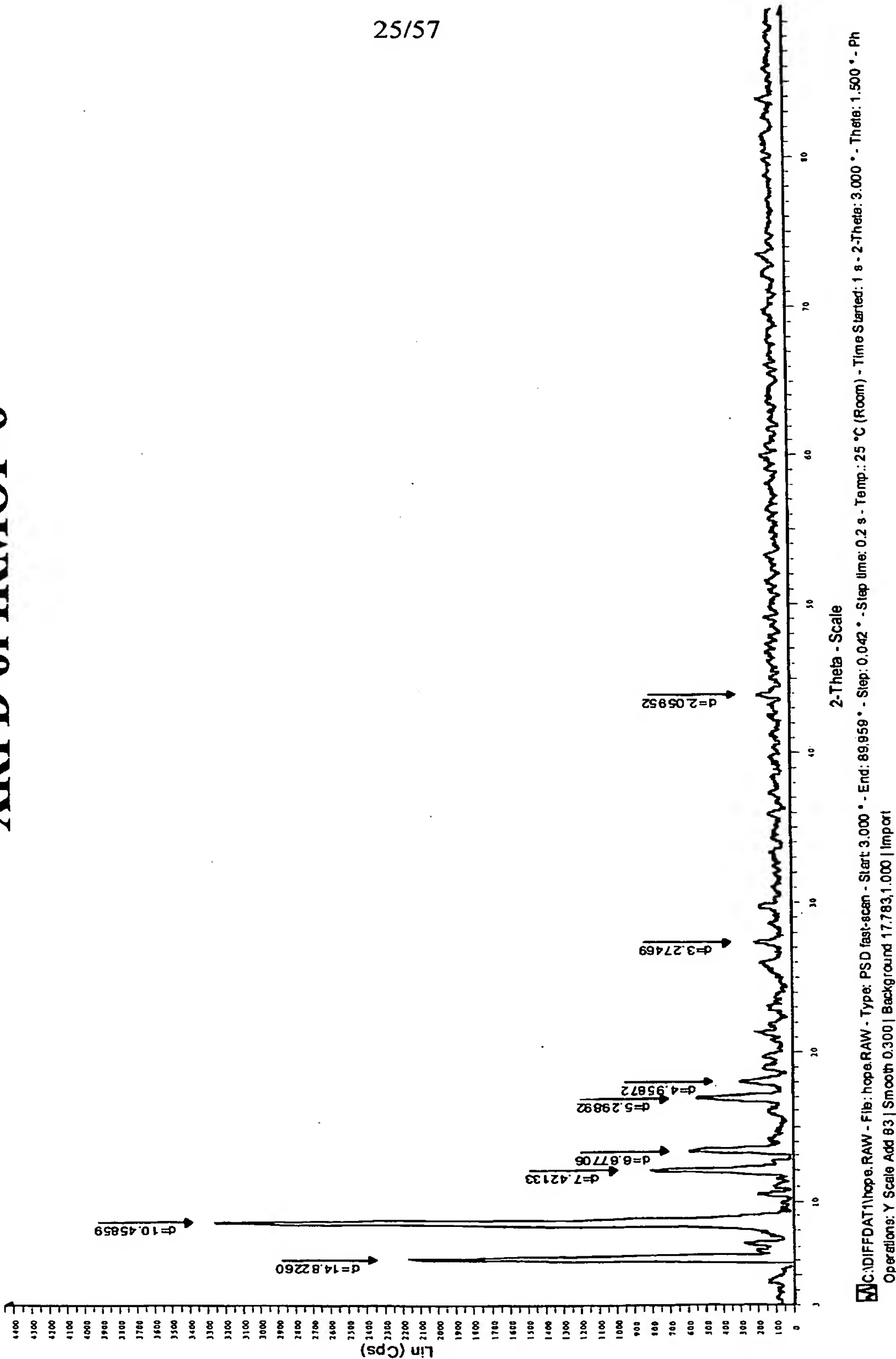
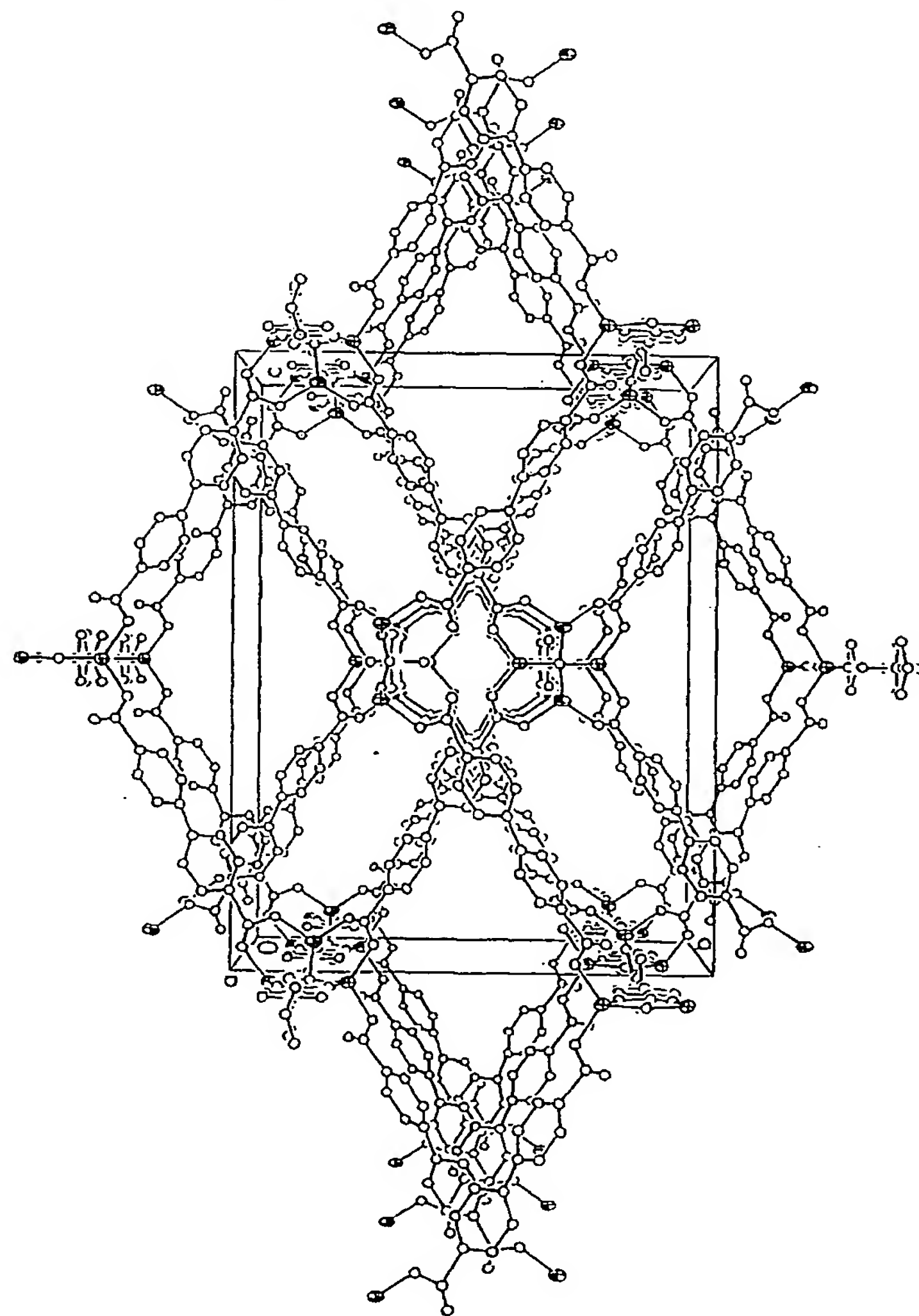


Figure 20

# Crystal Structure for IRMOF-9



## Crystal data

Orthorhombic, *Pnmm*

*a* = 17.128(4) Å

*b* = 20.001(4) Å

*c* = 27.305(6) Å

*V* = 9354(4) Å<sup>3</sup>

*R*1 = 0.1625 [*I* > 2σ(*I*)]

*wR*2 = 0.4304 (all data)

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Figure 21



# XRPD of IRMOF-9

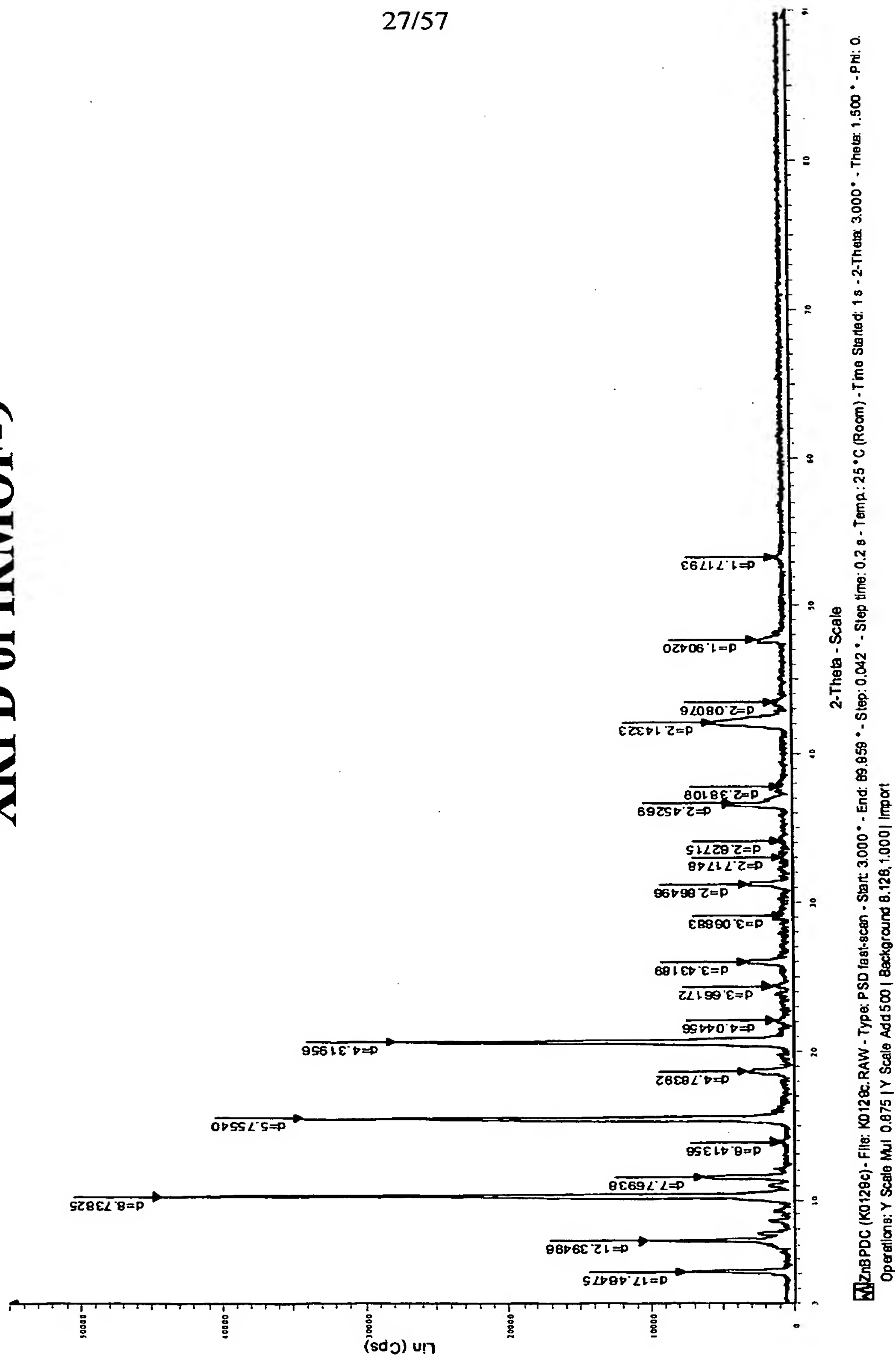


Figure 22a

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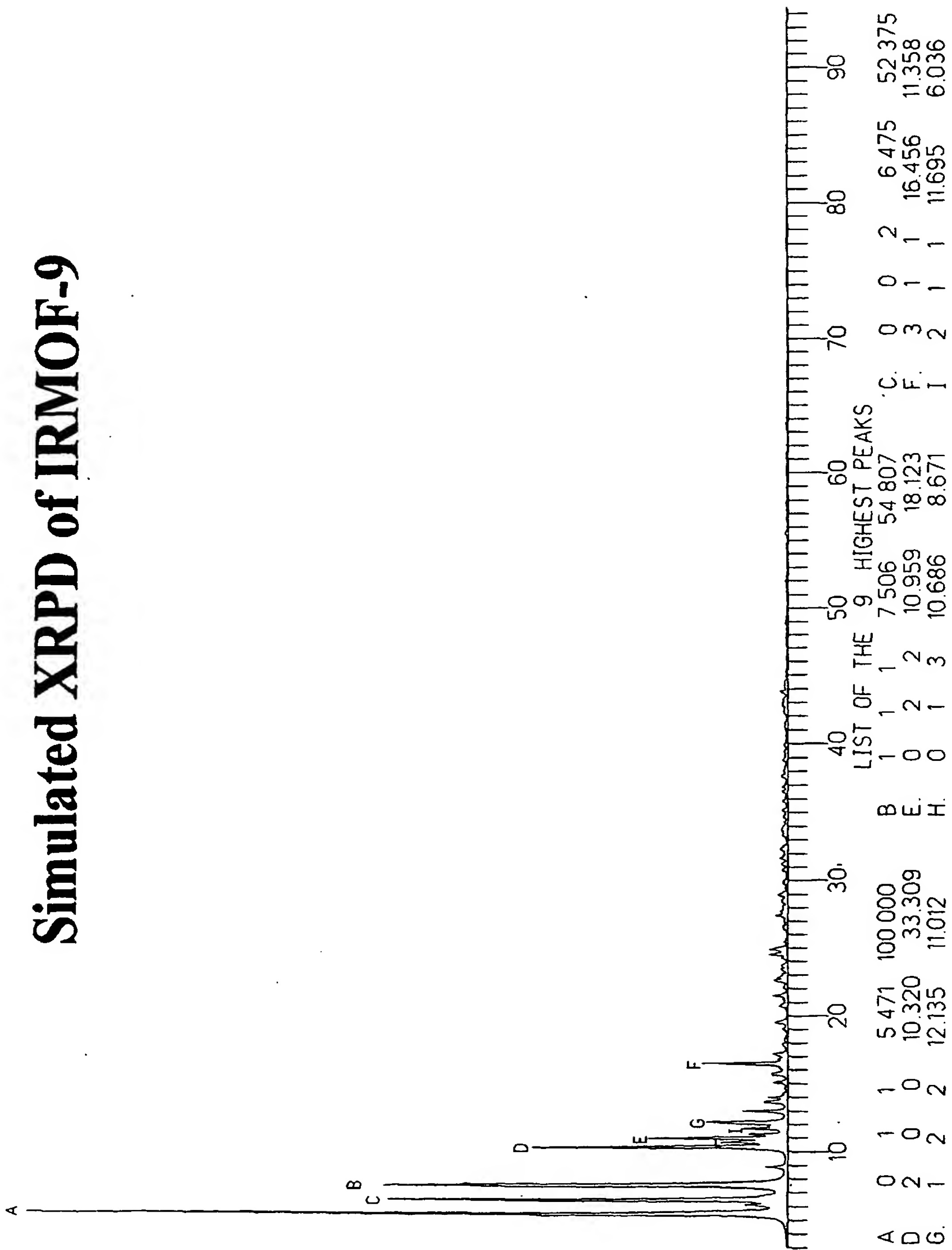


Figure 22b

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InfraRed spectrum for IRMOF-9

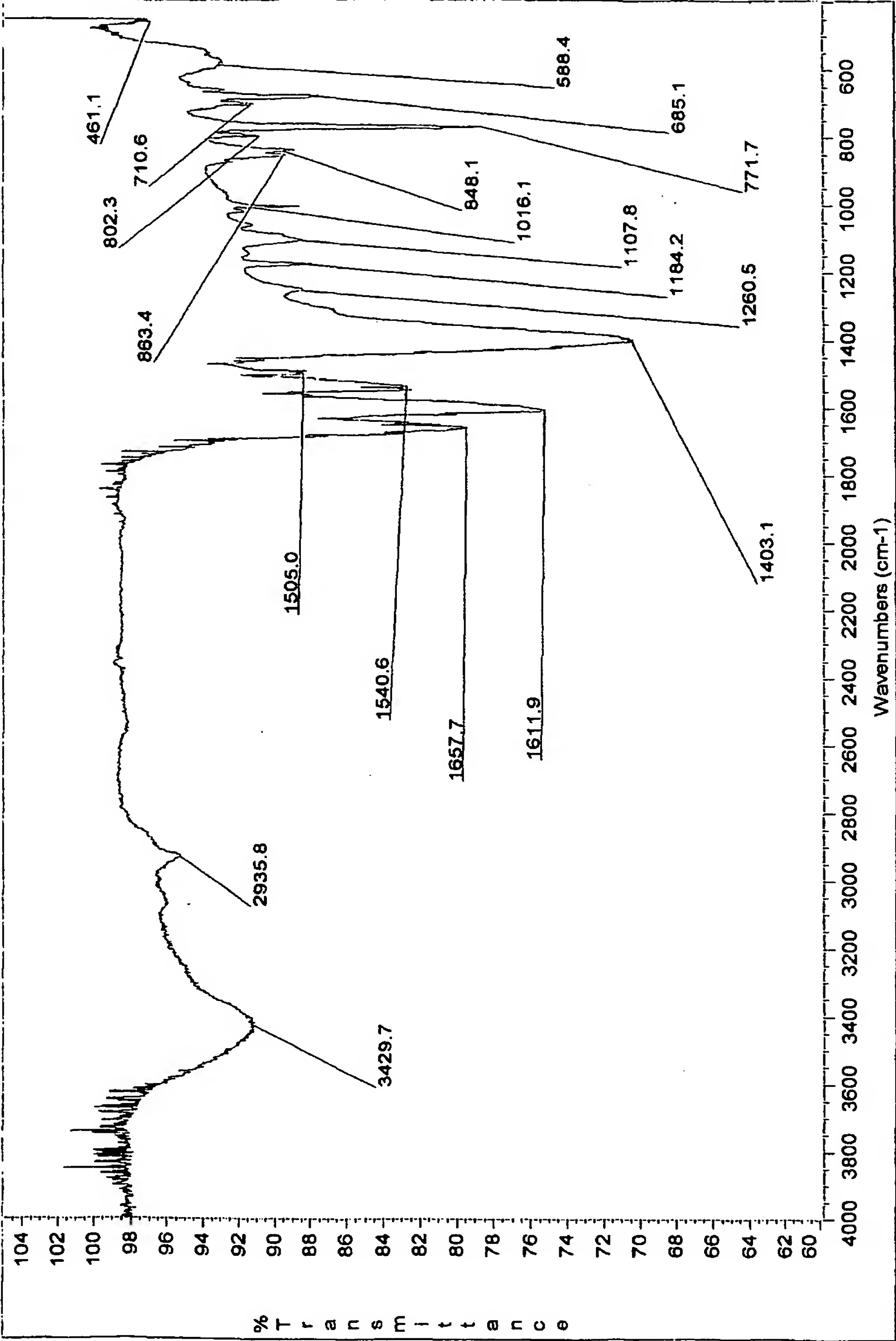
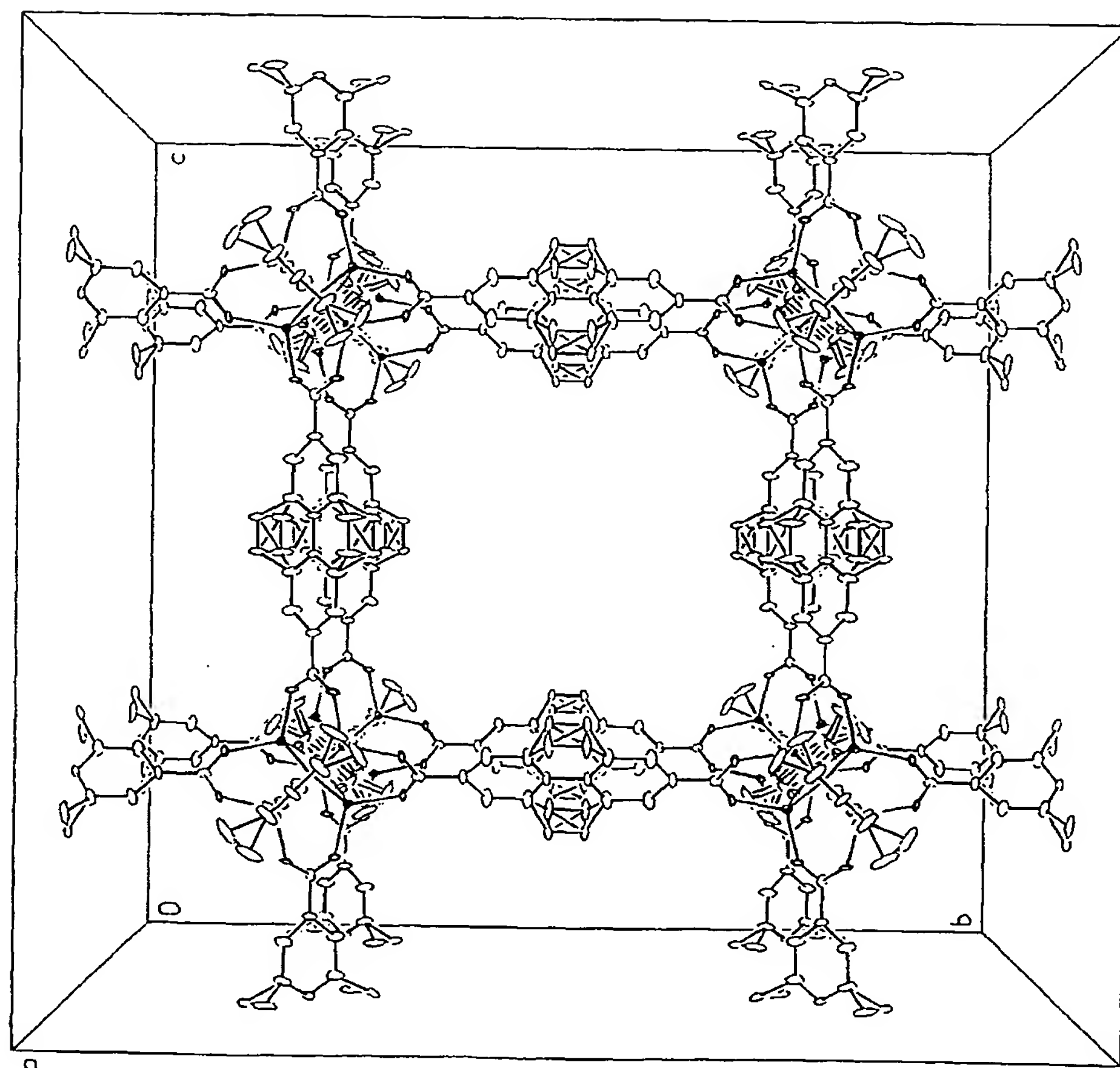


Figure 23

# Crystal Structure for IRMOF-12



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**Crystal data**  
**Cubic, *Fm3m***  
***a* = 34.2807(18) Å**  
***V* = 40286(4) Å<sup>3</sup>**  
***R*1 = 0.1080 [*I* > 2σ(*I*)]**  
***wR*2 = 0.3875 (all data)**

**Figure 24**

XRPD of IRMOF-12

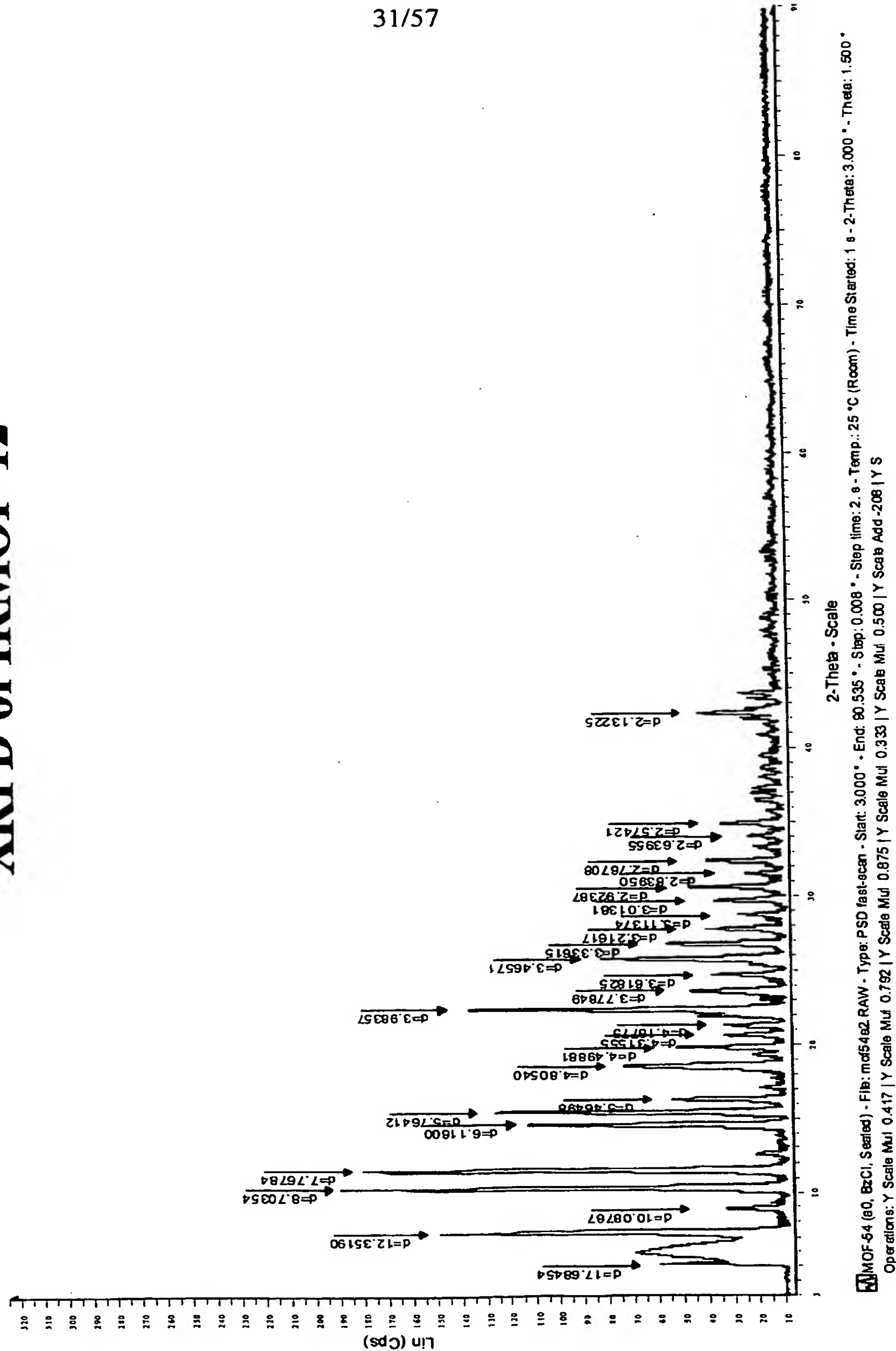


Figure 25a

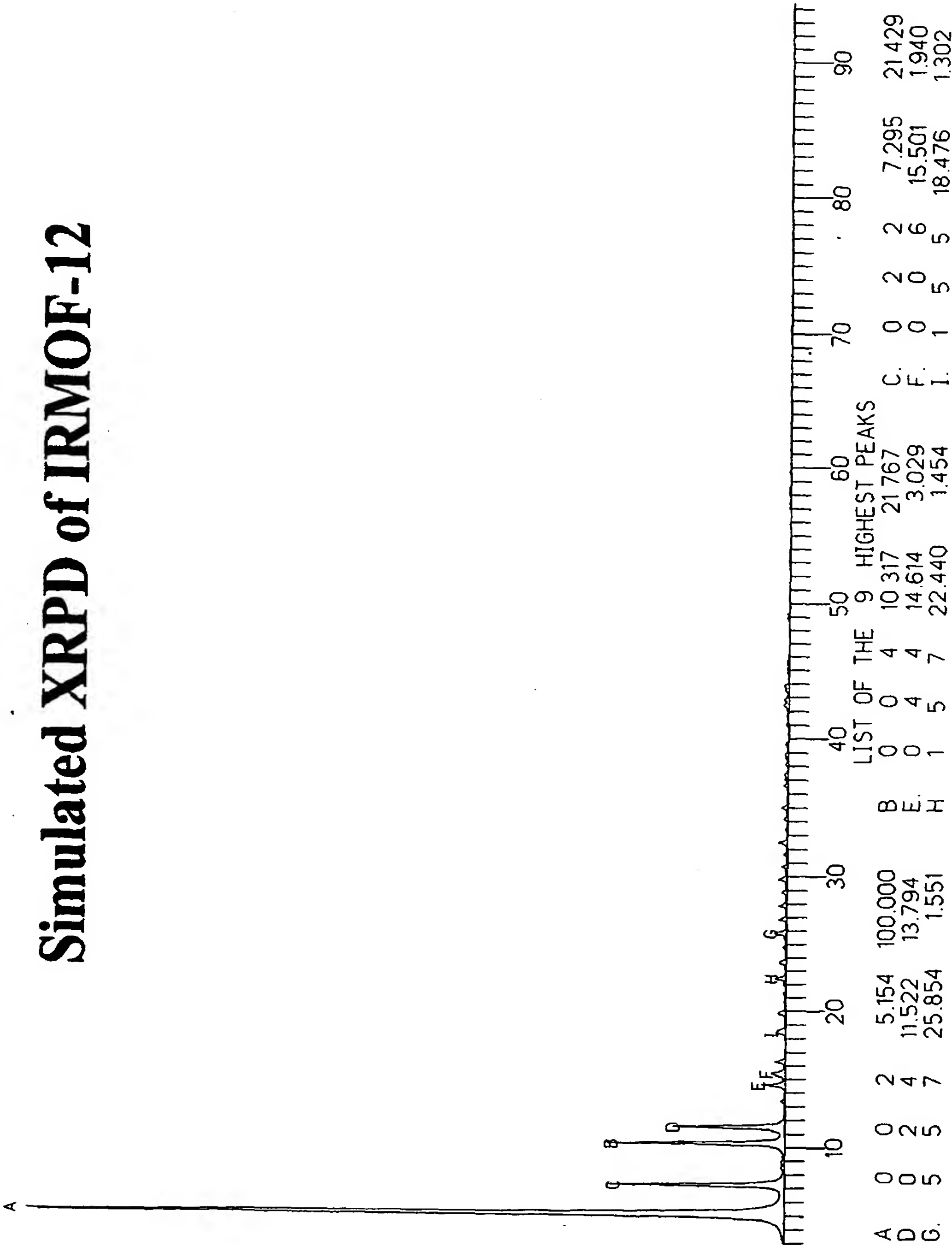


Figure 25b

InfraRed spectrum for IRMOF-12

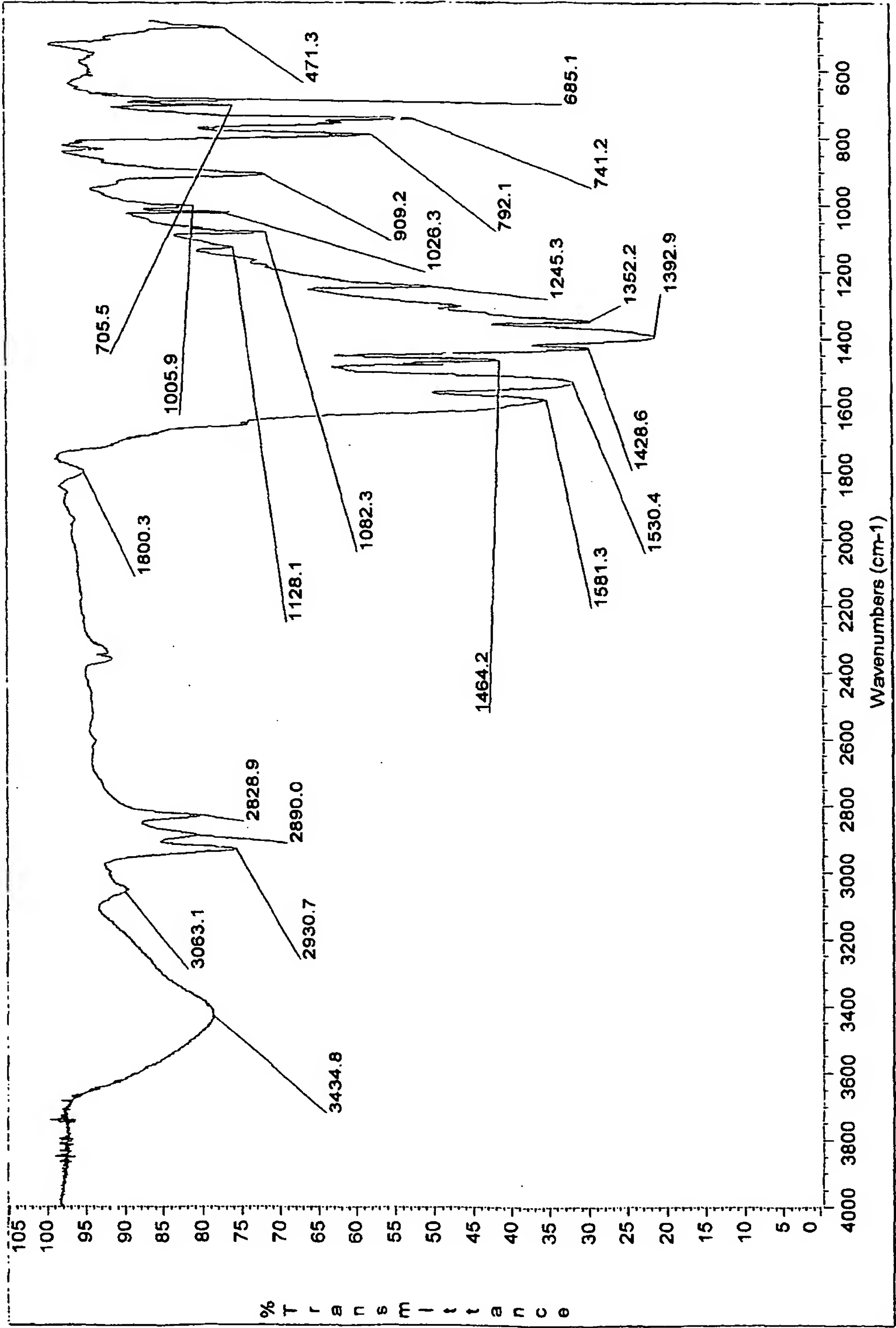
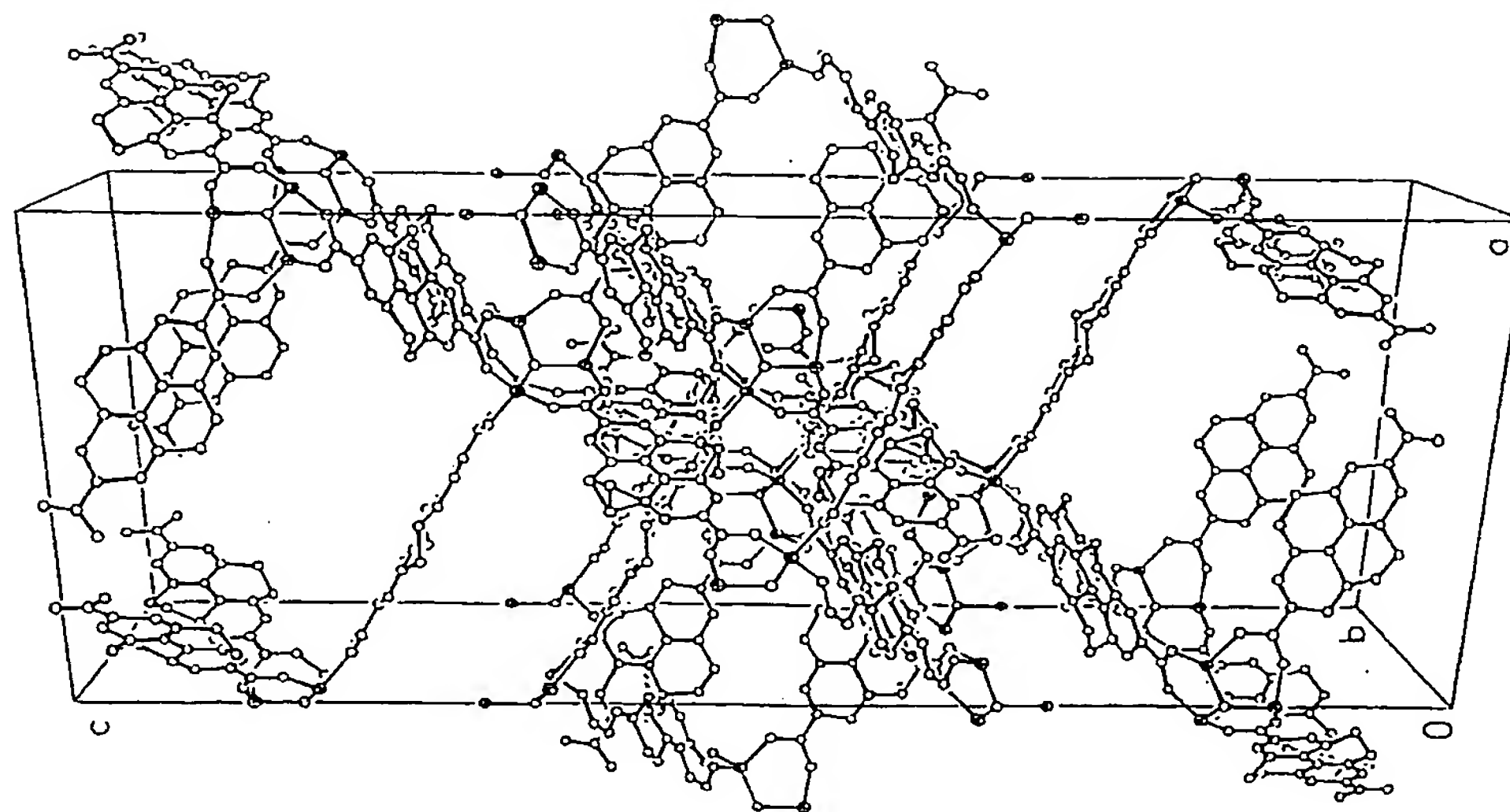


Figure 26



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# Crystal Structure for IRMOF-11



**Crystal data**  
**Rhombohedral(H),  $R3m$**   
 **$a = 24.938(2) \text{ \AA}$**   
 **$c = 54.521(6) \text{ \AA}$**   
 **$V = 29365(4) \text{ \AA}^3$**   
 **$R1 = 0.1995 [I > 2\sigma(I)]$**   
 **$wR2 = 0.5602$  (all data)**

**Figure 27**

# XRPD of IRMOF-11

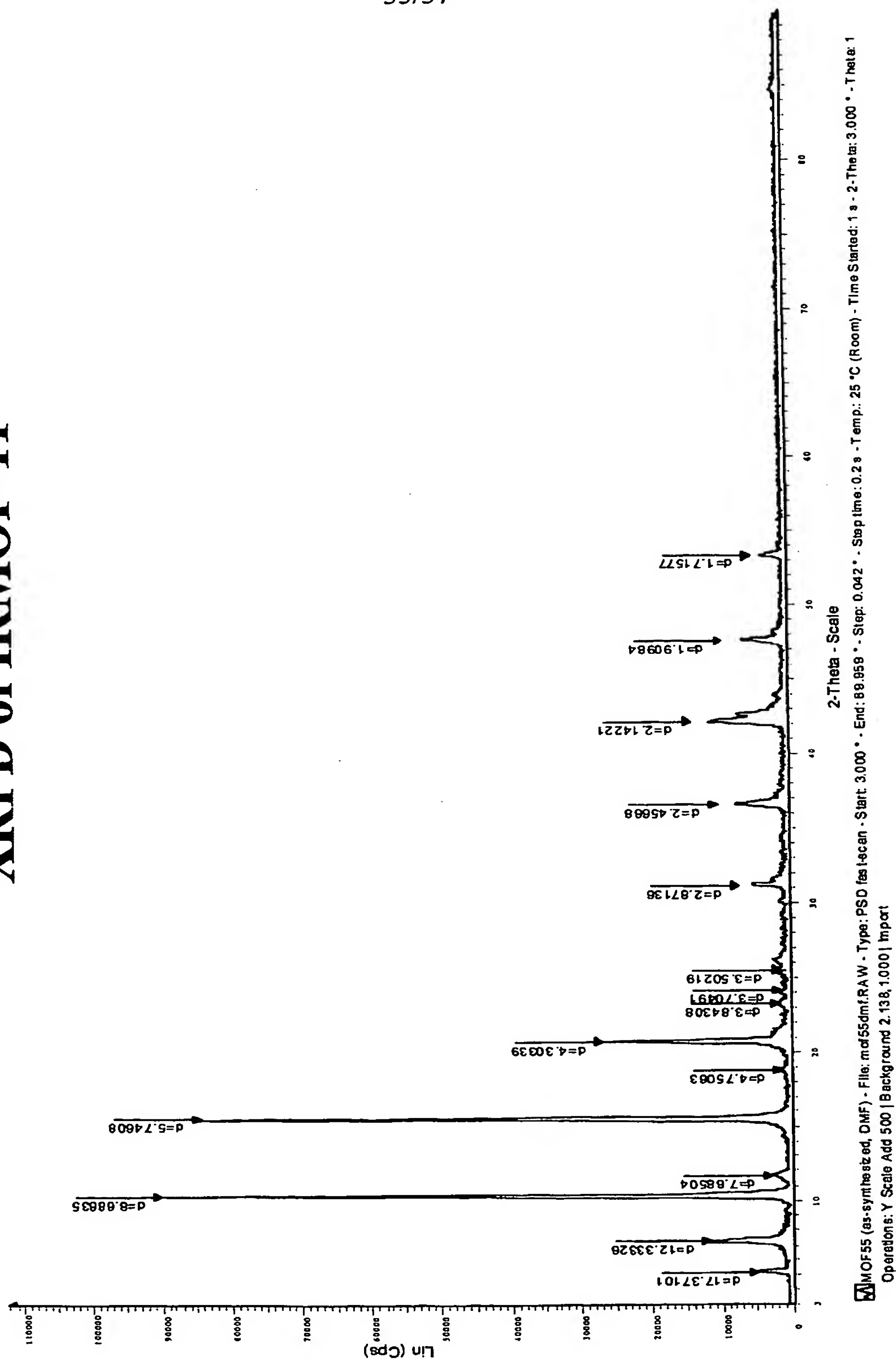


Figure 28a

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# Simulated XRPD of IRMOF-11

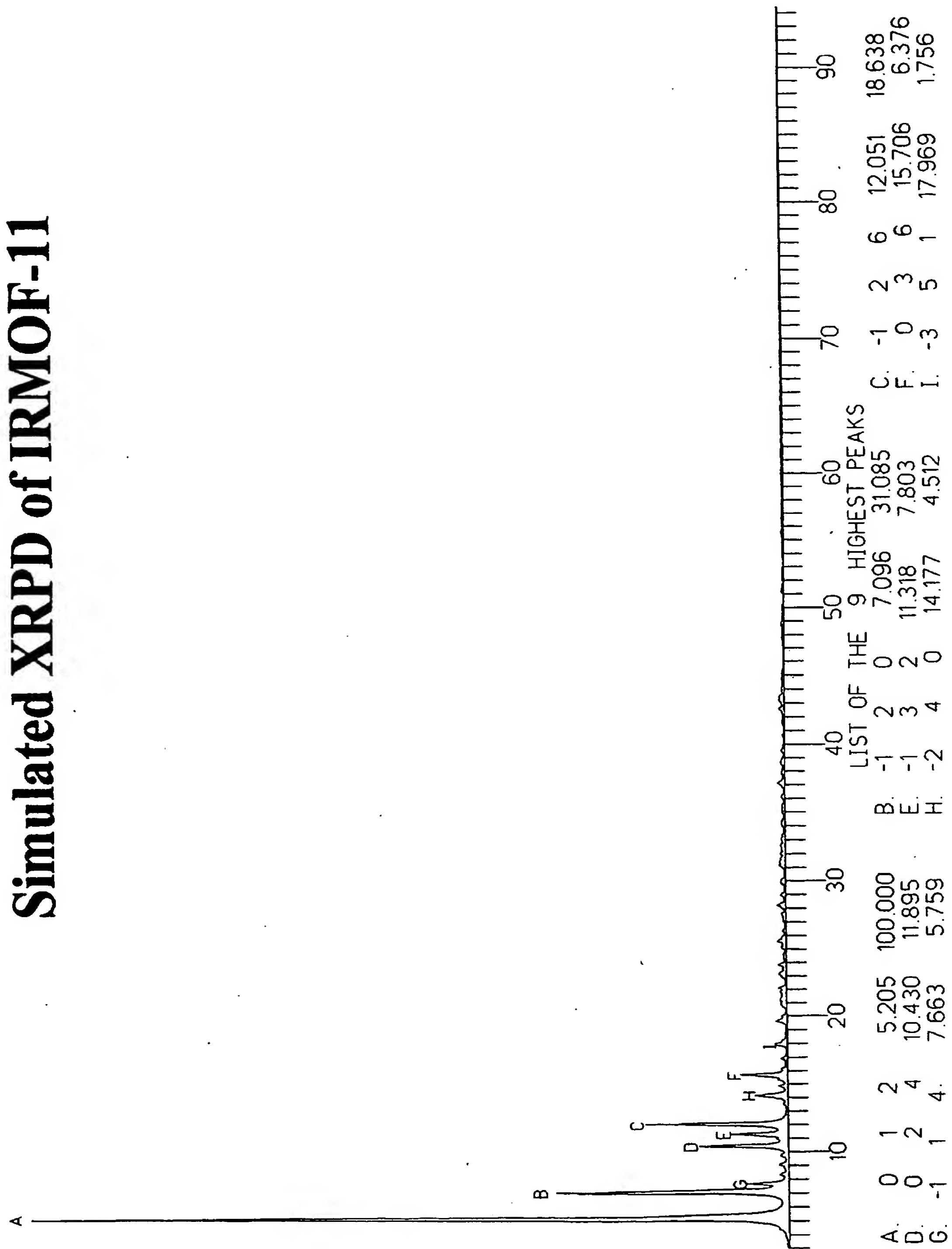


Figure 28b

# InfraRed spectrum for IRMOF-11

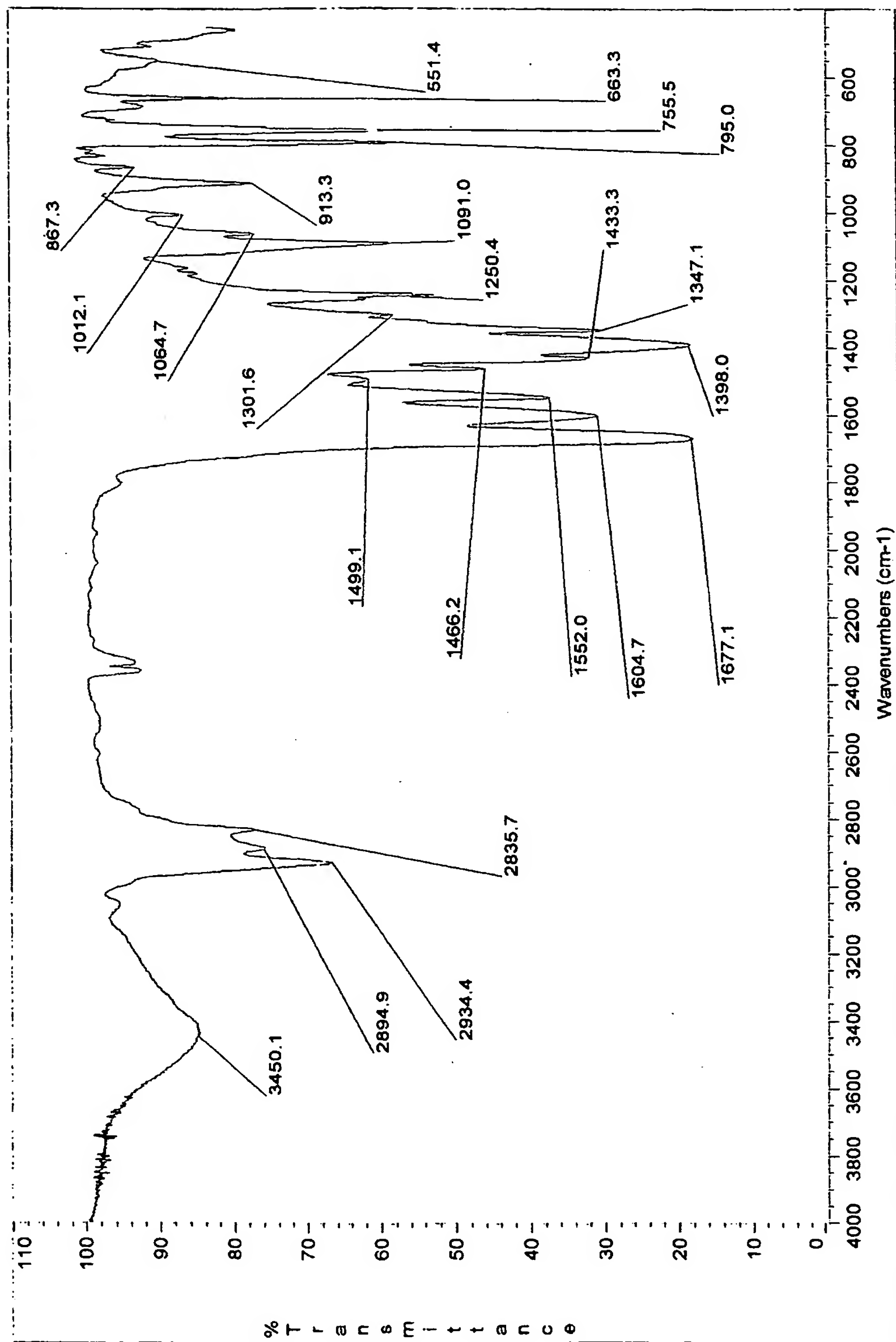


Figure 29

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Crystal data  
Cubic,  $Fm\bar{3}m$   
 $a = 34.396 \text{ \AA}$   
 $V = 40693 \text{ \AA}^3$

## Crystal Structure for IRMOF-14

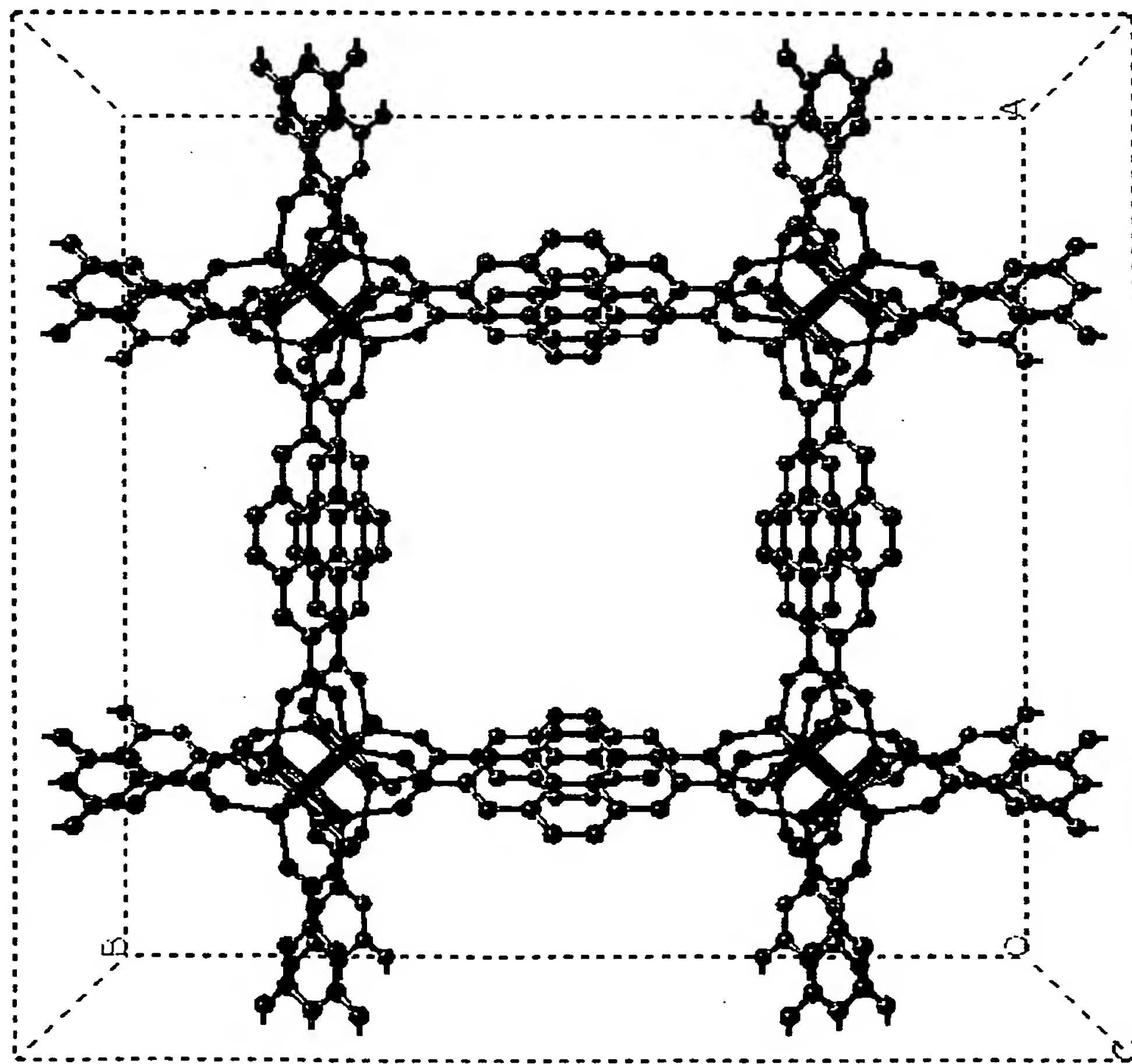


Figure 30

XRPD of IRMOF-14

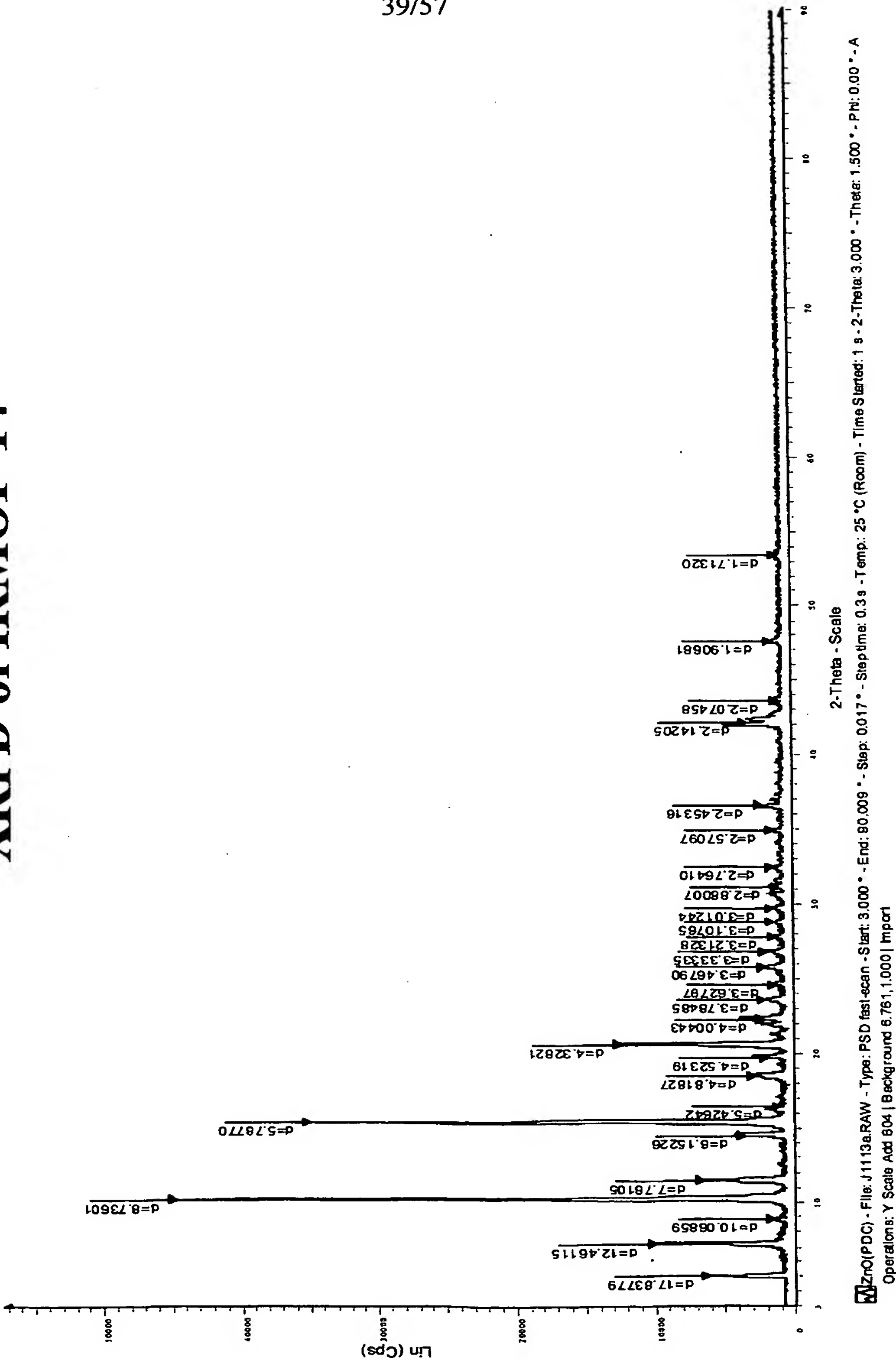


Figure 31a

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# Simulated XRPD of IRMOF-14

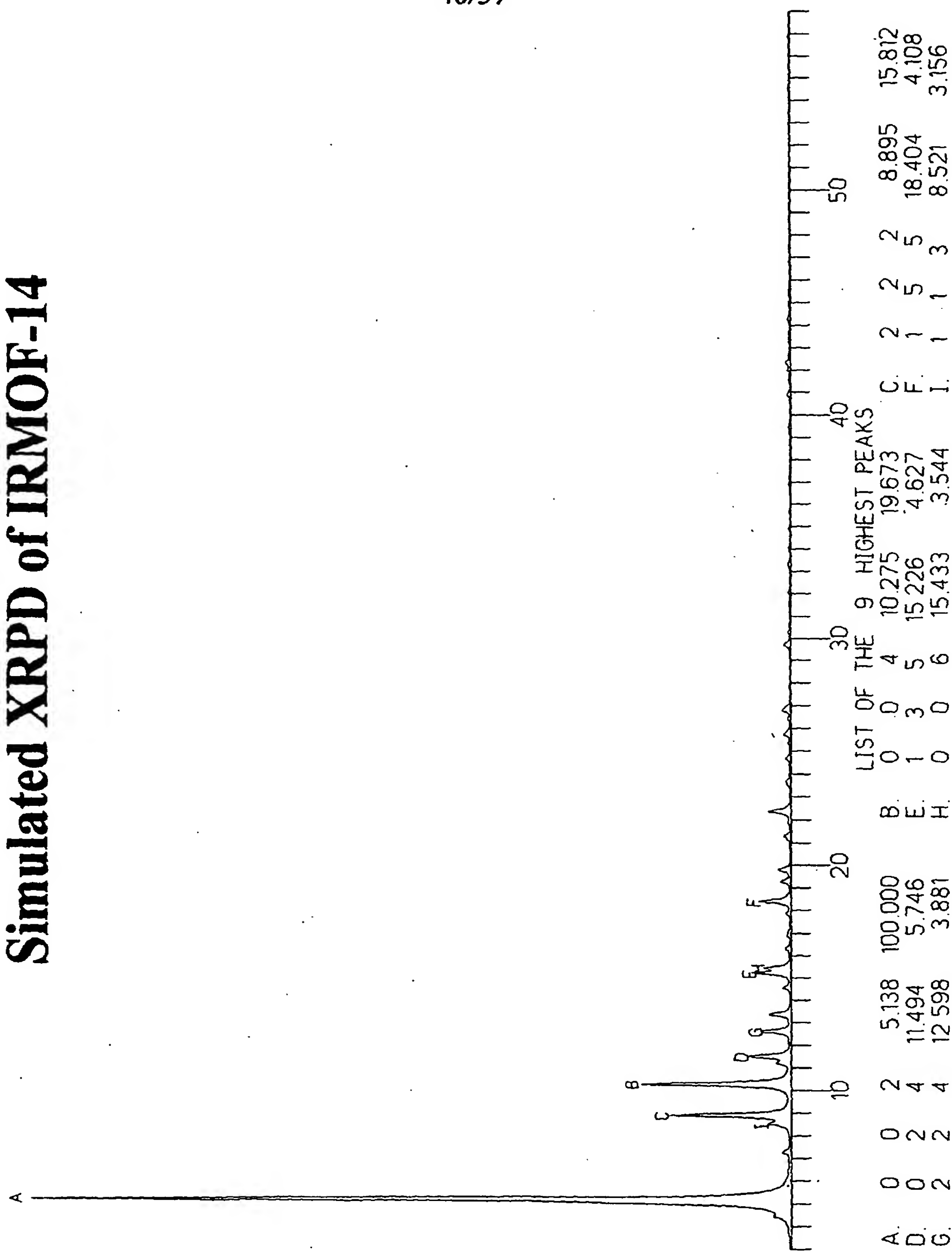


Figure 31b



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InfraRed spectrum for IRMOF-14

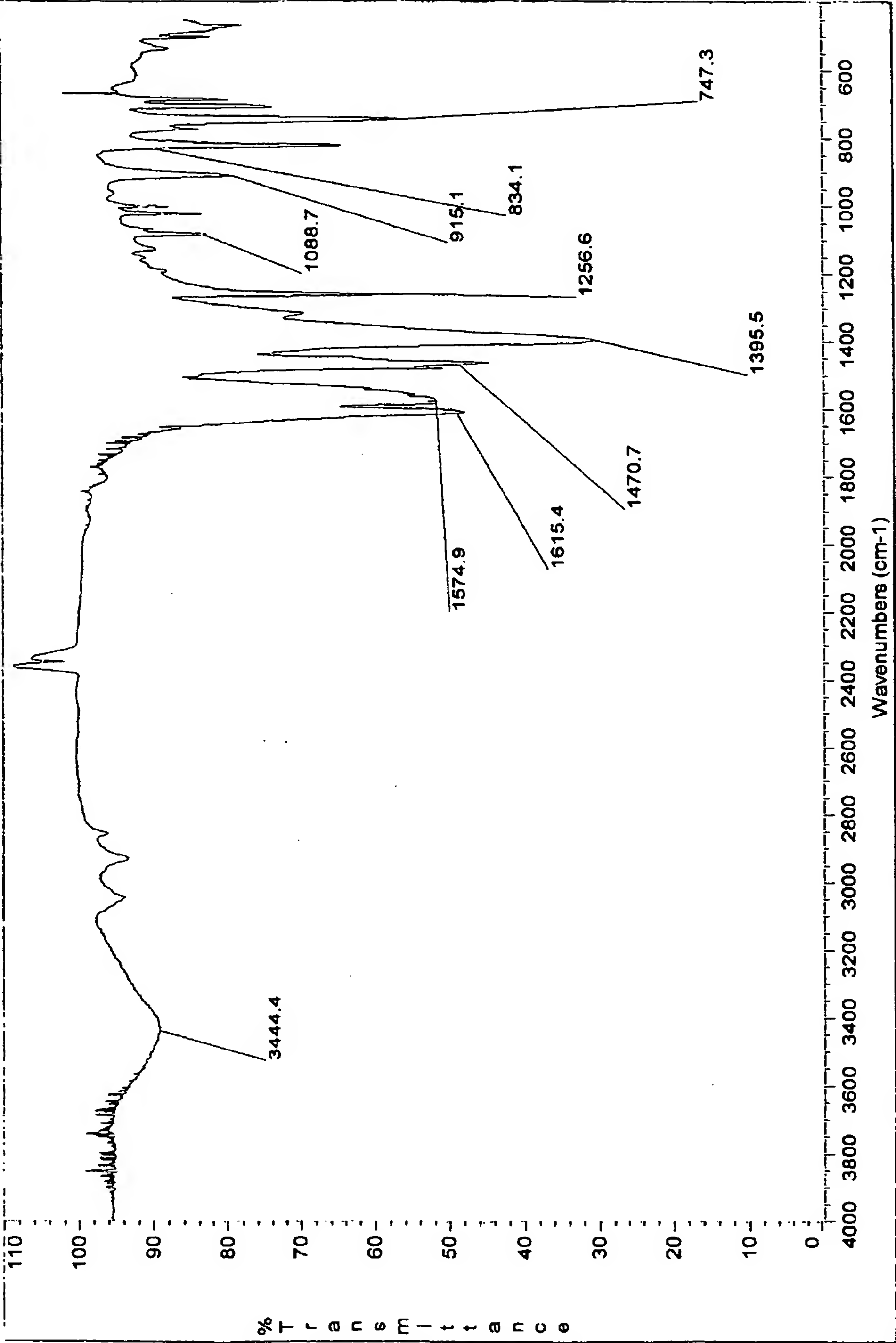


Figure 32

XRPD of IRMOF-13

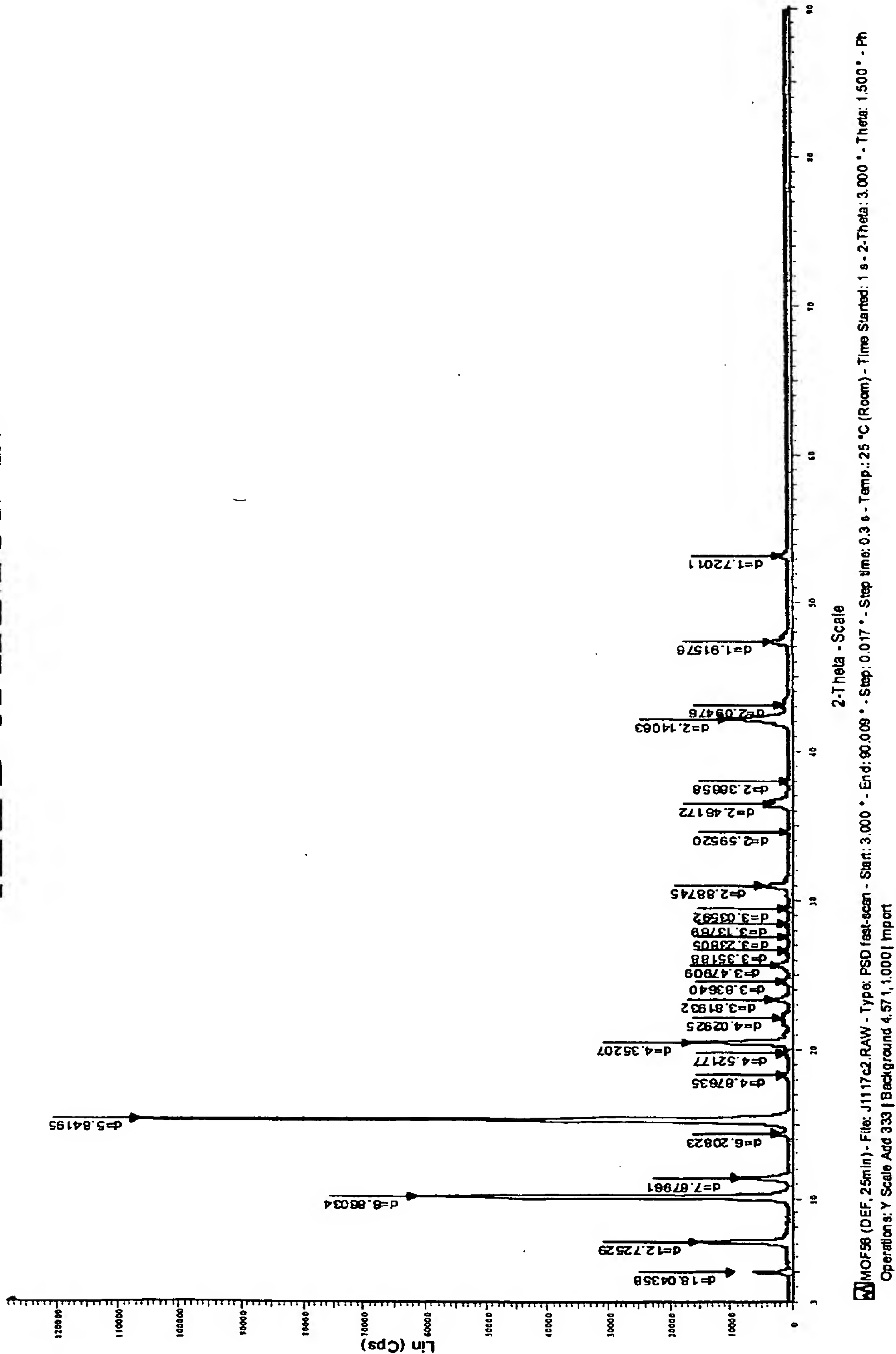


Figure 33

# InfraRed spectrum for IRMOF-13

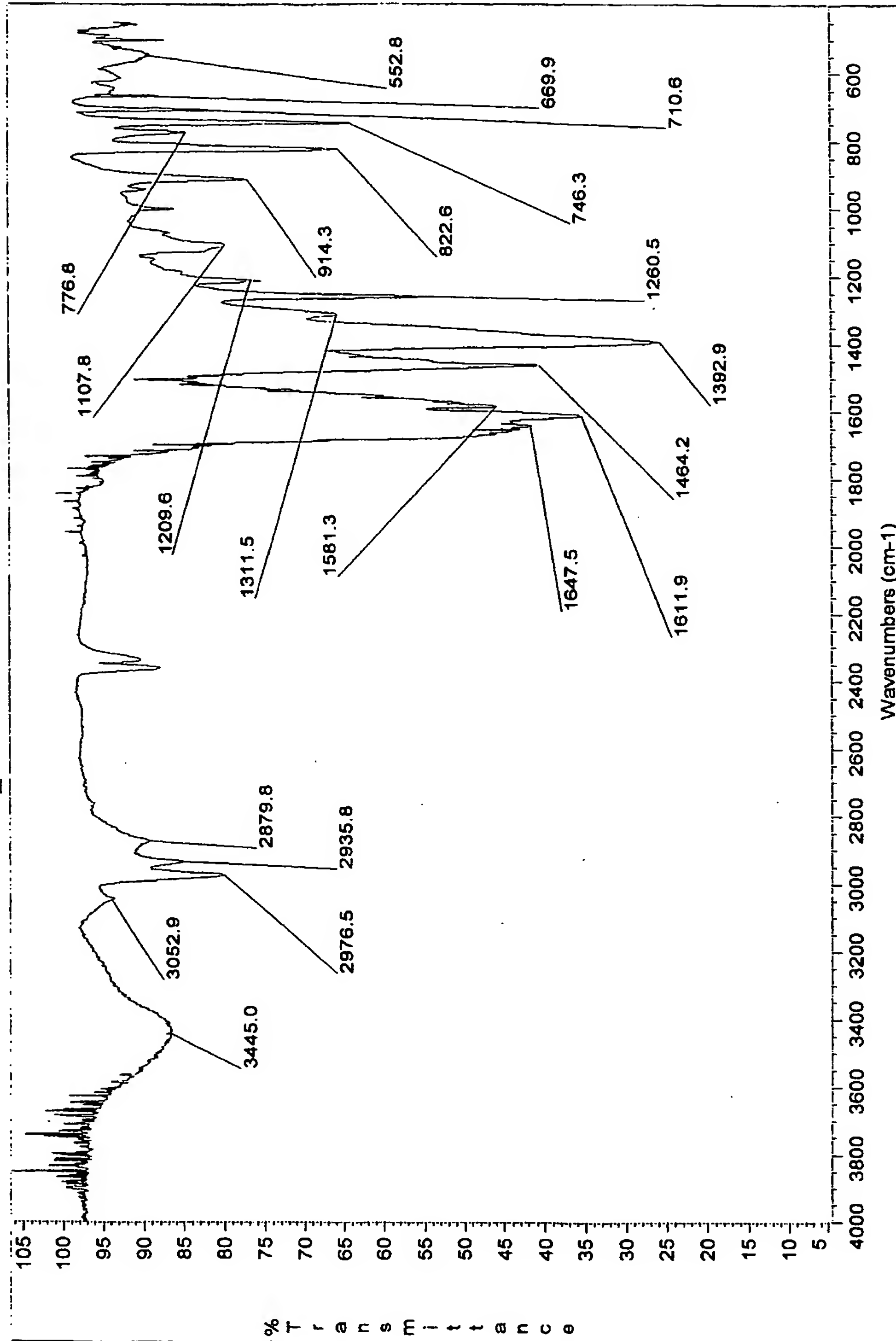


Figure 34

XRPD of IRMOF-15

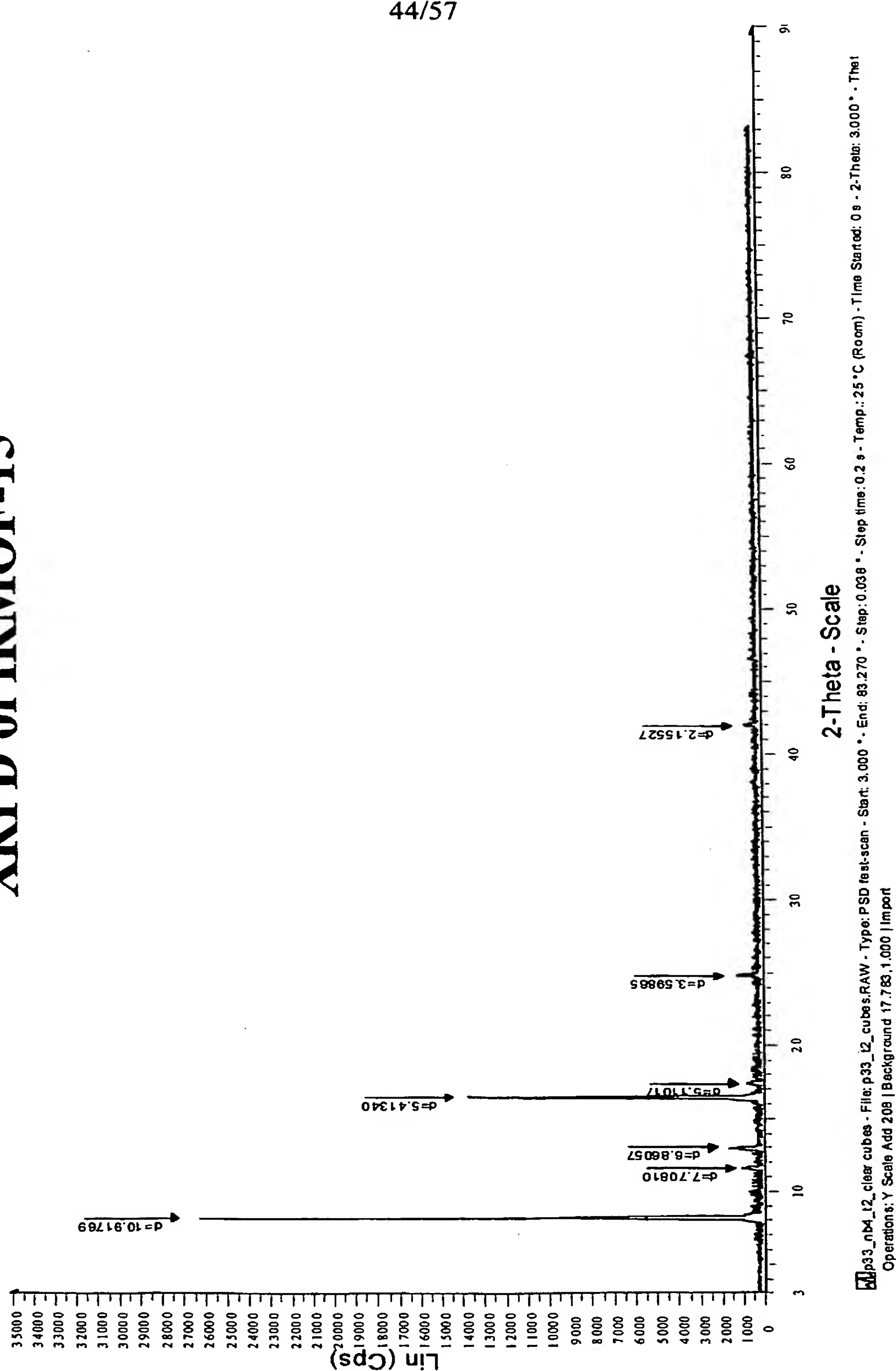


Figure 35

# InfraRed spectrum for IRMOF-15

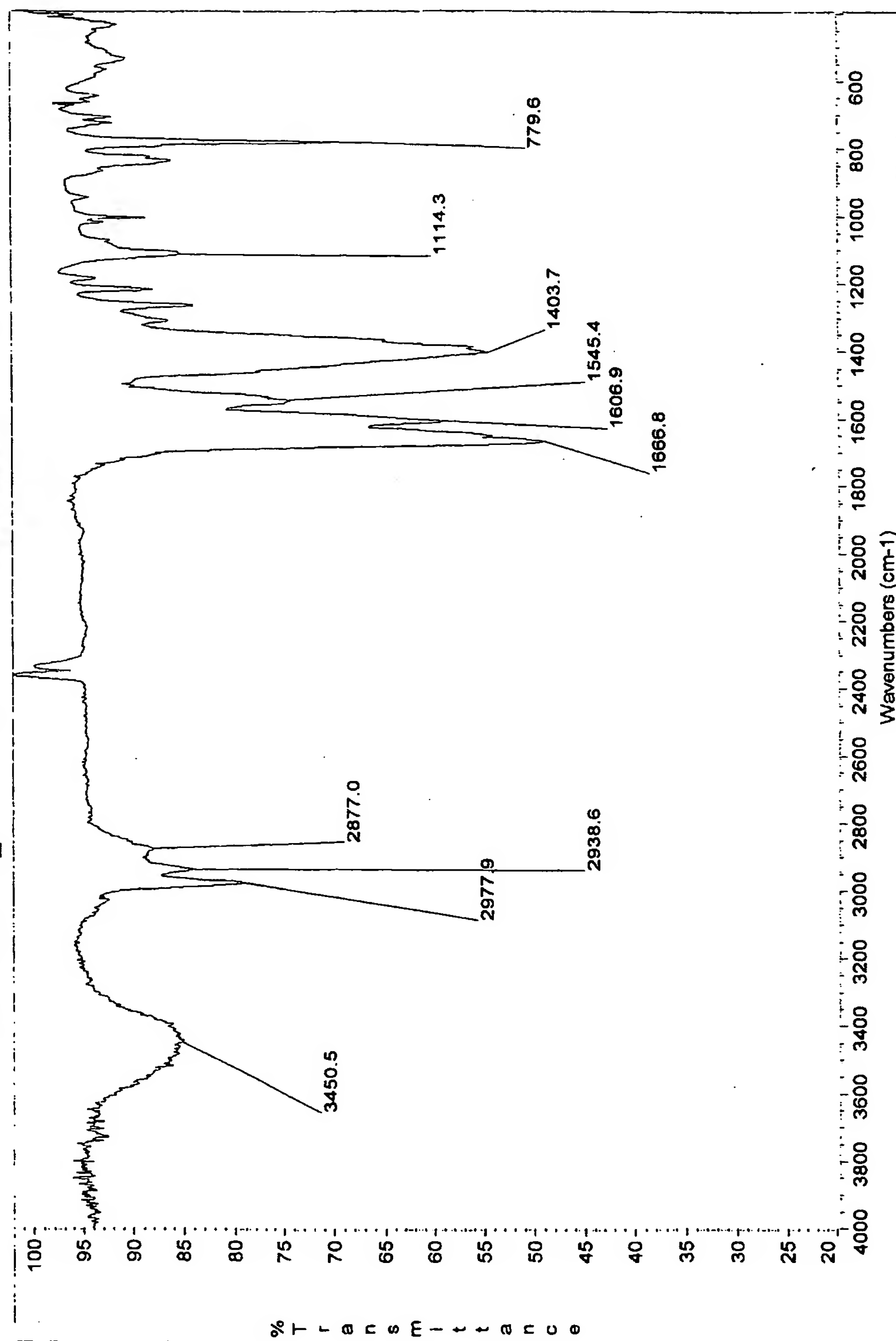


Figure 36

Table 1: Sorption data for IRMOF-3, Zn<sub>4</sub>O (H<sub>2</sub>NBDC)<sub>3</sub>

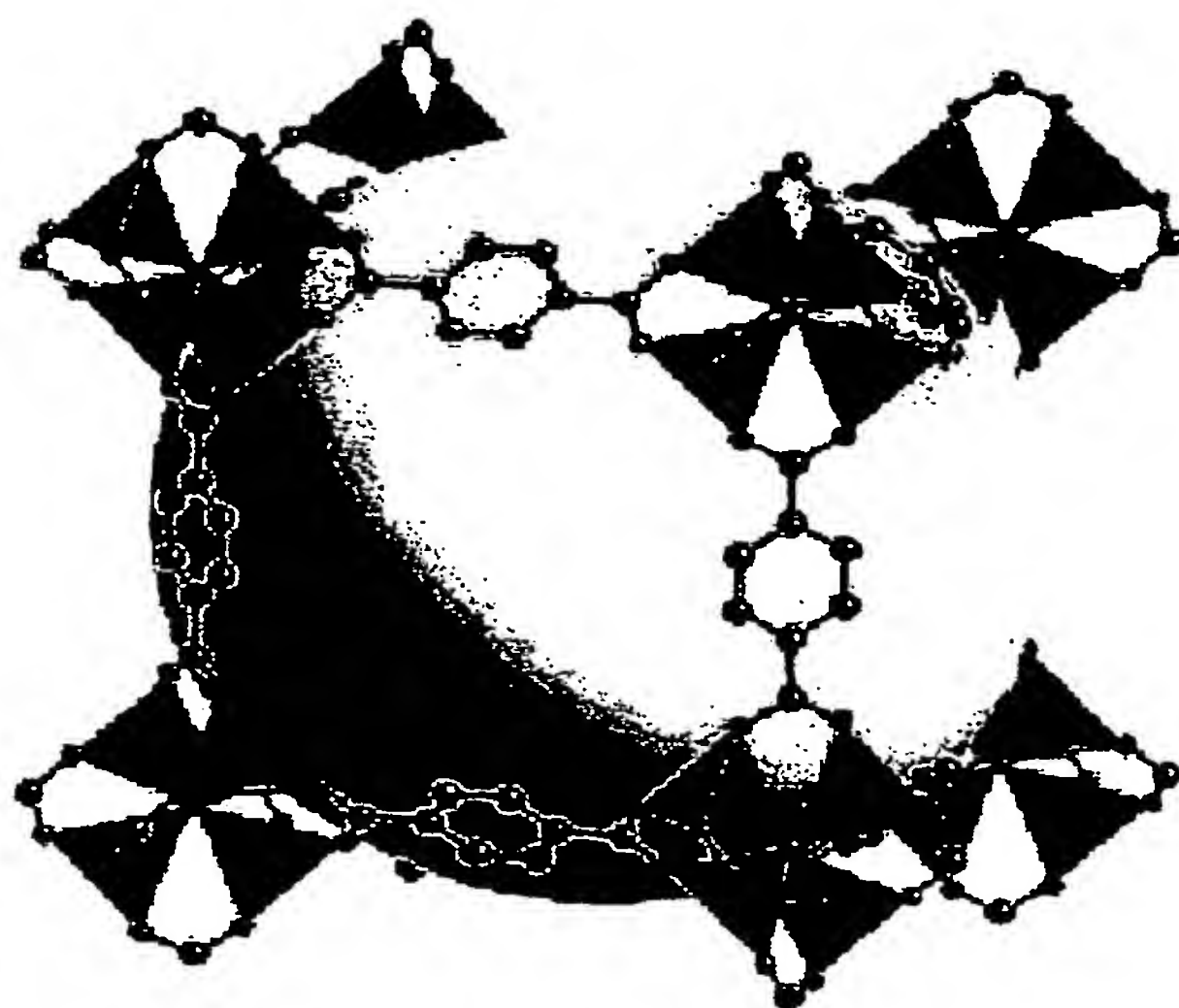
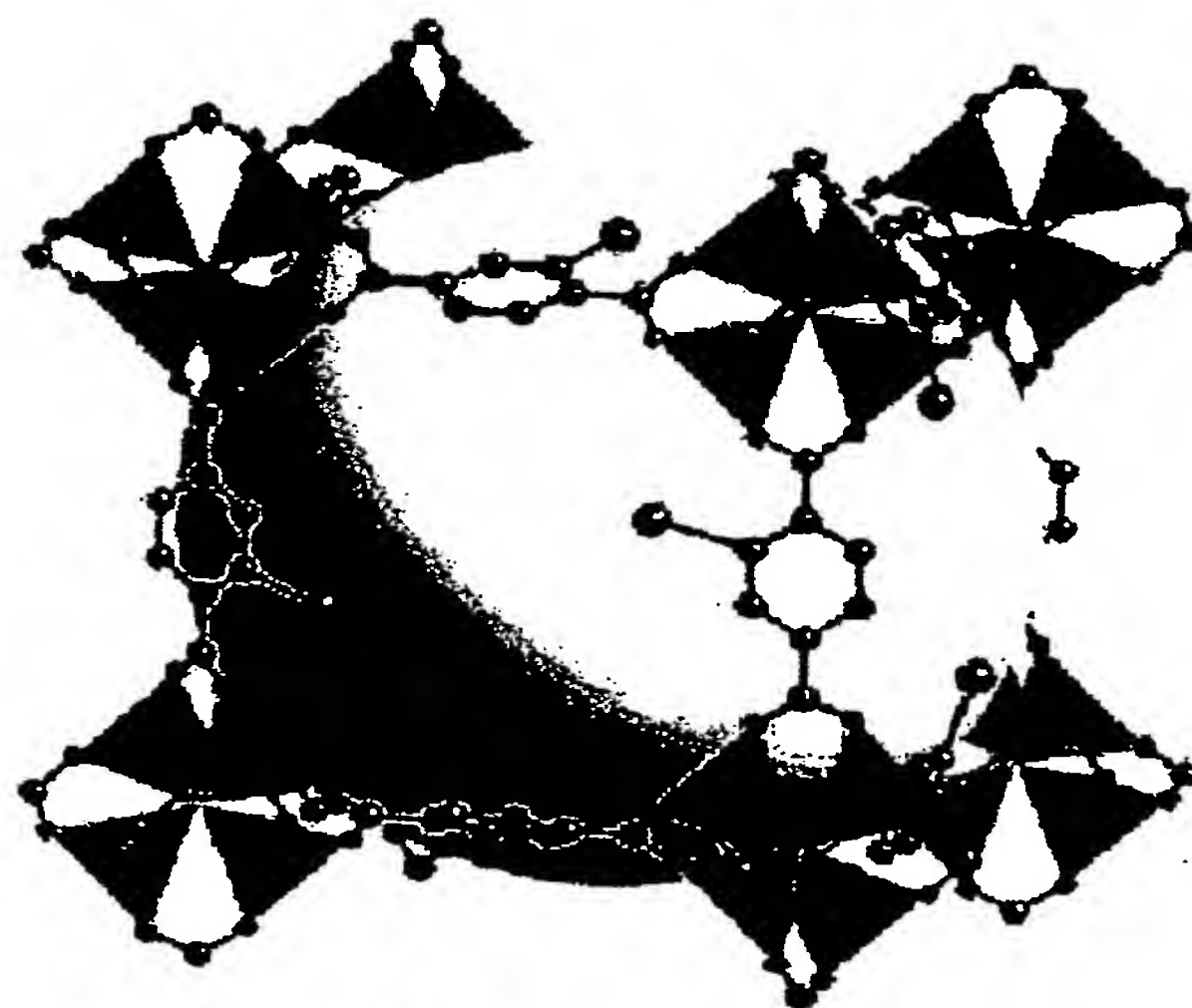
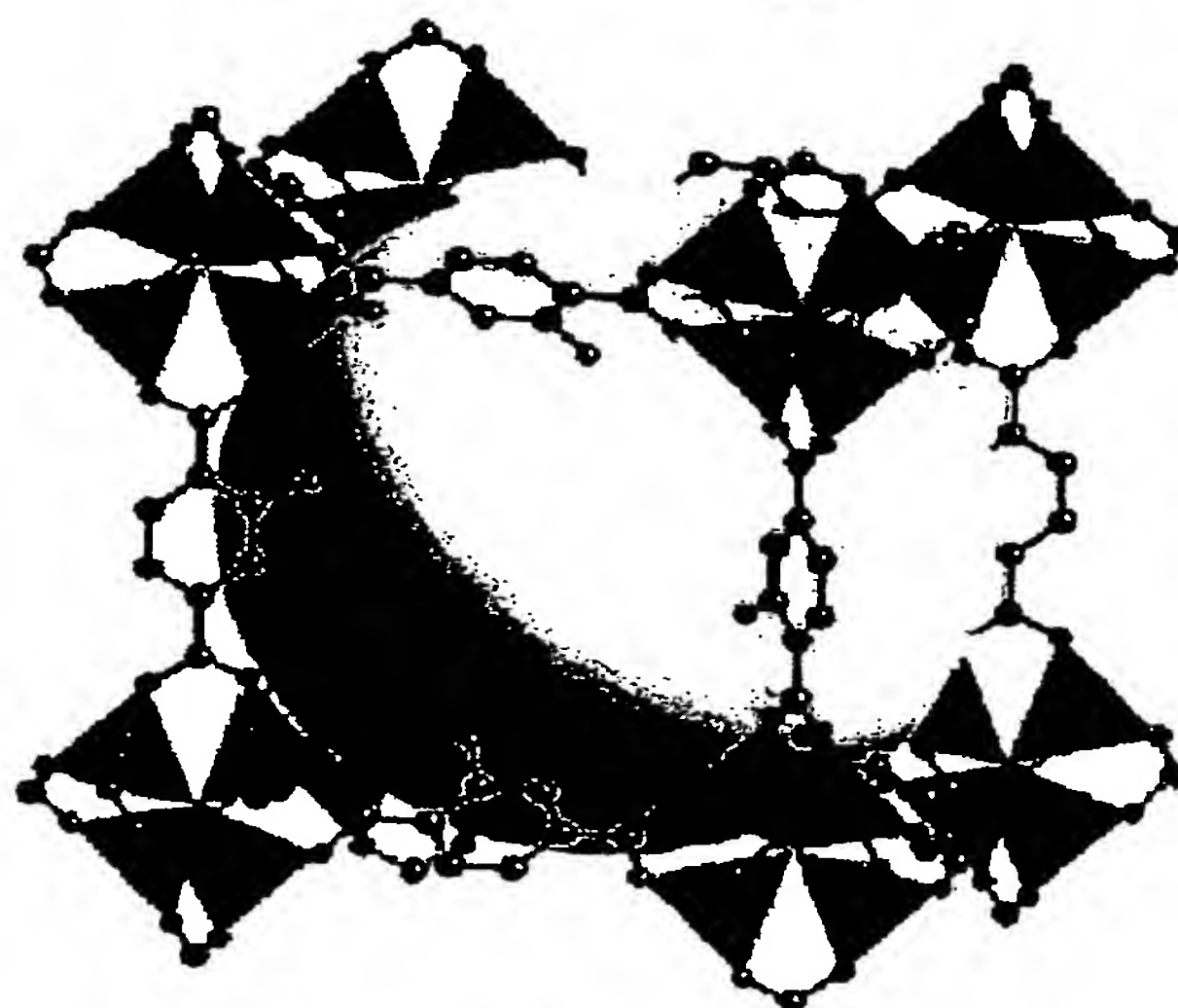
Sorbate	W (mg/g)	Guest/UC	V (cm <sup>3</sup> /g)	V (cm <sup>3</sup> /cm <sup>3</sup> )
N <sub>2</sub>	775	180	0.95	0.59
CH <sub>2</sub> Cl <sub>2</sub>	1073	83	0.83	0.52
C <sub>6</sub> H <sub>6</sub>	748	63	0.85	0.53
CCl <sub>4</sub>	1371	58	0.85	0.53
C <sub>6</sub> H <sub>12</sub>	625	48	0.82	0.52

Table 2 : Sorption data for IRMOF-6, Zn<sub>4</sub>O ([C<sub>2</sub>H<sub>4</sub>]BDC)<sub>3</sub>

Sorbate	W (mg/g)	Guest/UC	V (cm <sup>3</sup> /g)	V (cm <sup>3</sup> /cm <sup>3</sup> )
N <sub>2</sub>	750	182	0.93	0.60
CH <sub>2</sub> Cl <sub>2</sub>	1170	93	0.88	0.57
C <sub>6</sub> H <sub>6</sub>	800	69	0.90	0.58
CCl <sub>4</sub>	1397	62	0.88	0.57
C <sub>6</sub> H <sub>12</sub>	705	57	0.90	0.58

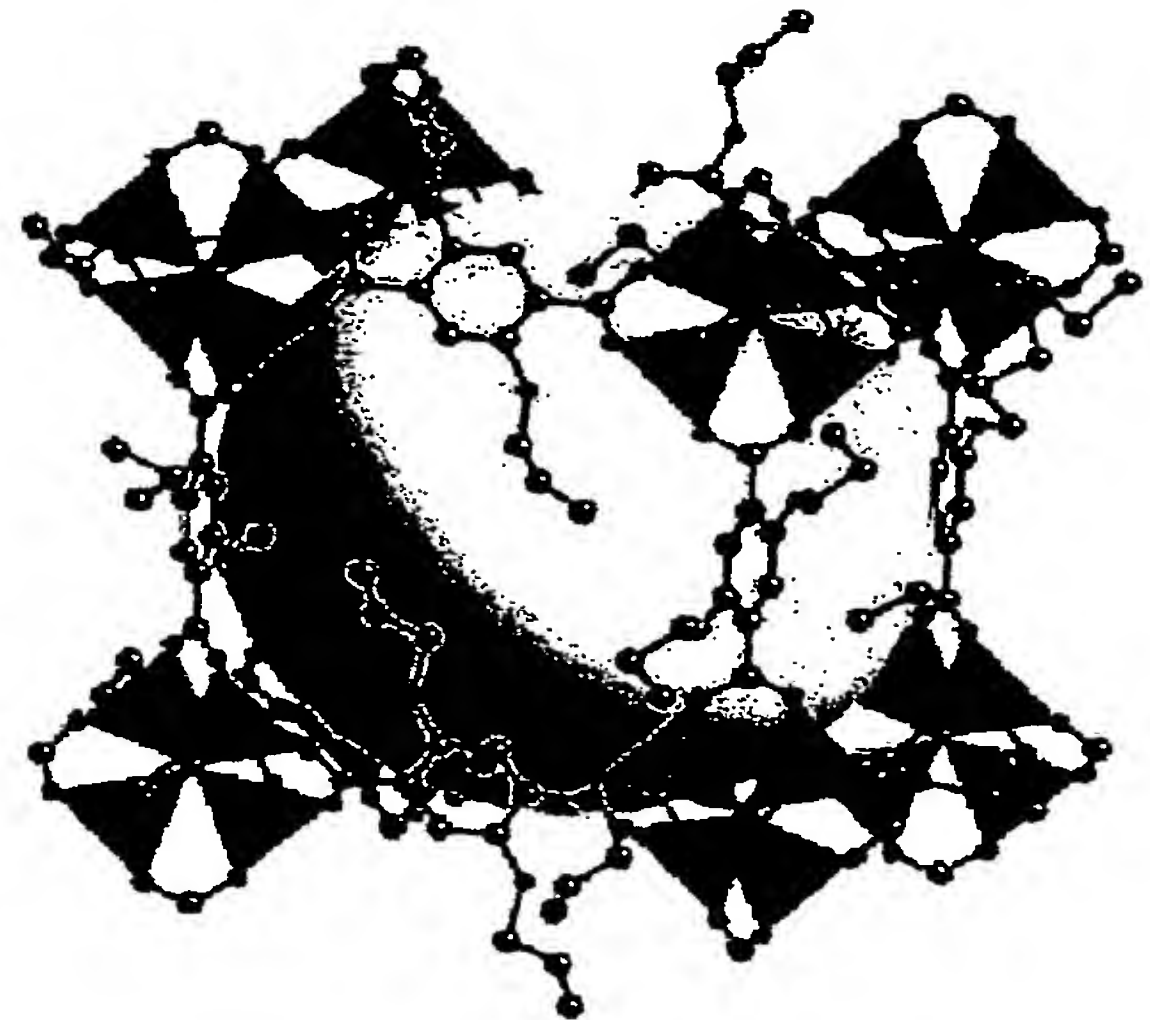


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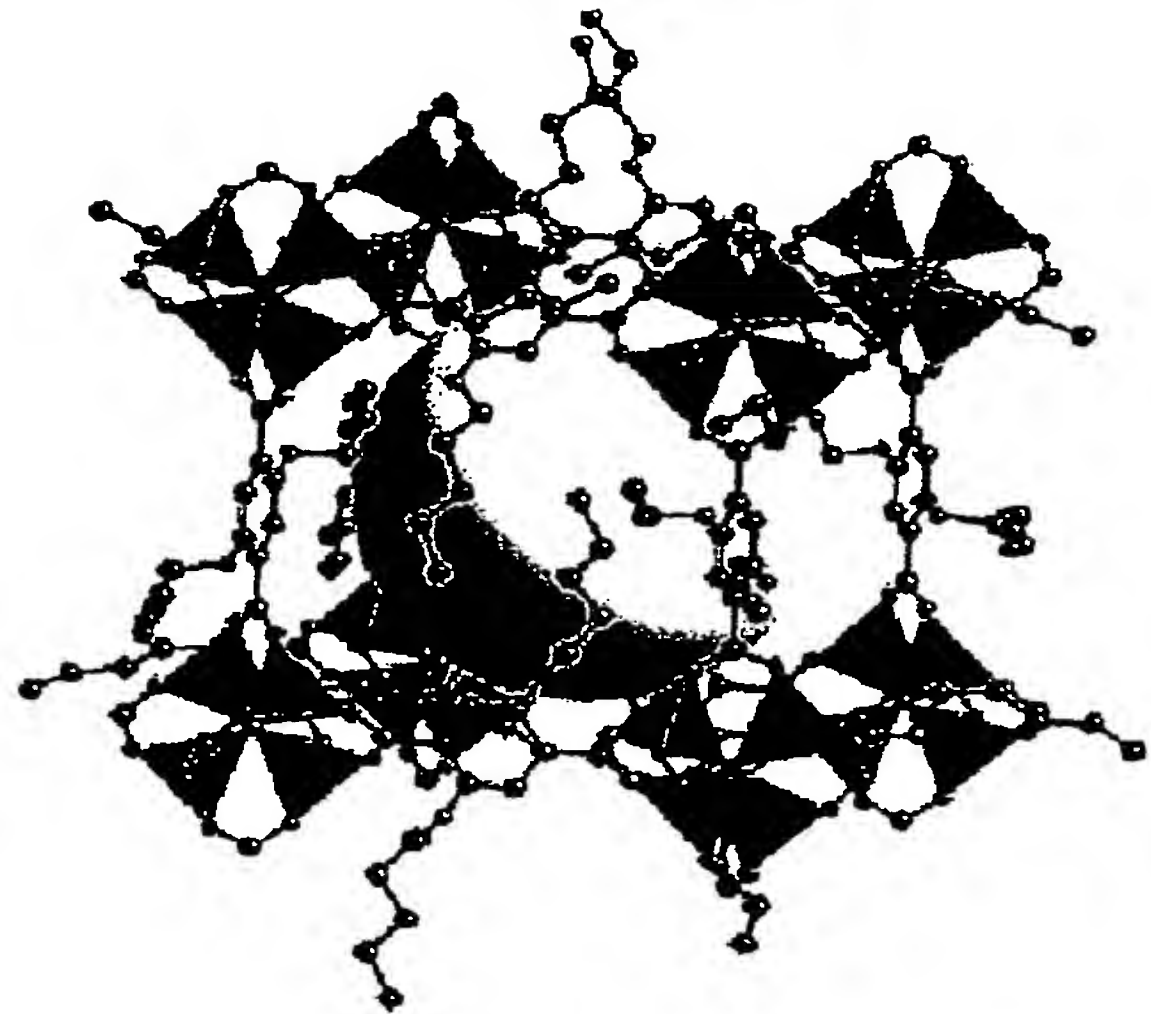
**Figure 37****Figure 38****Figure 39**

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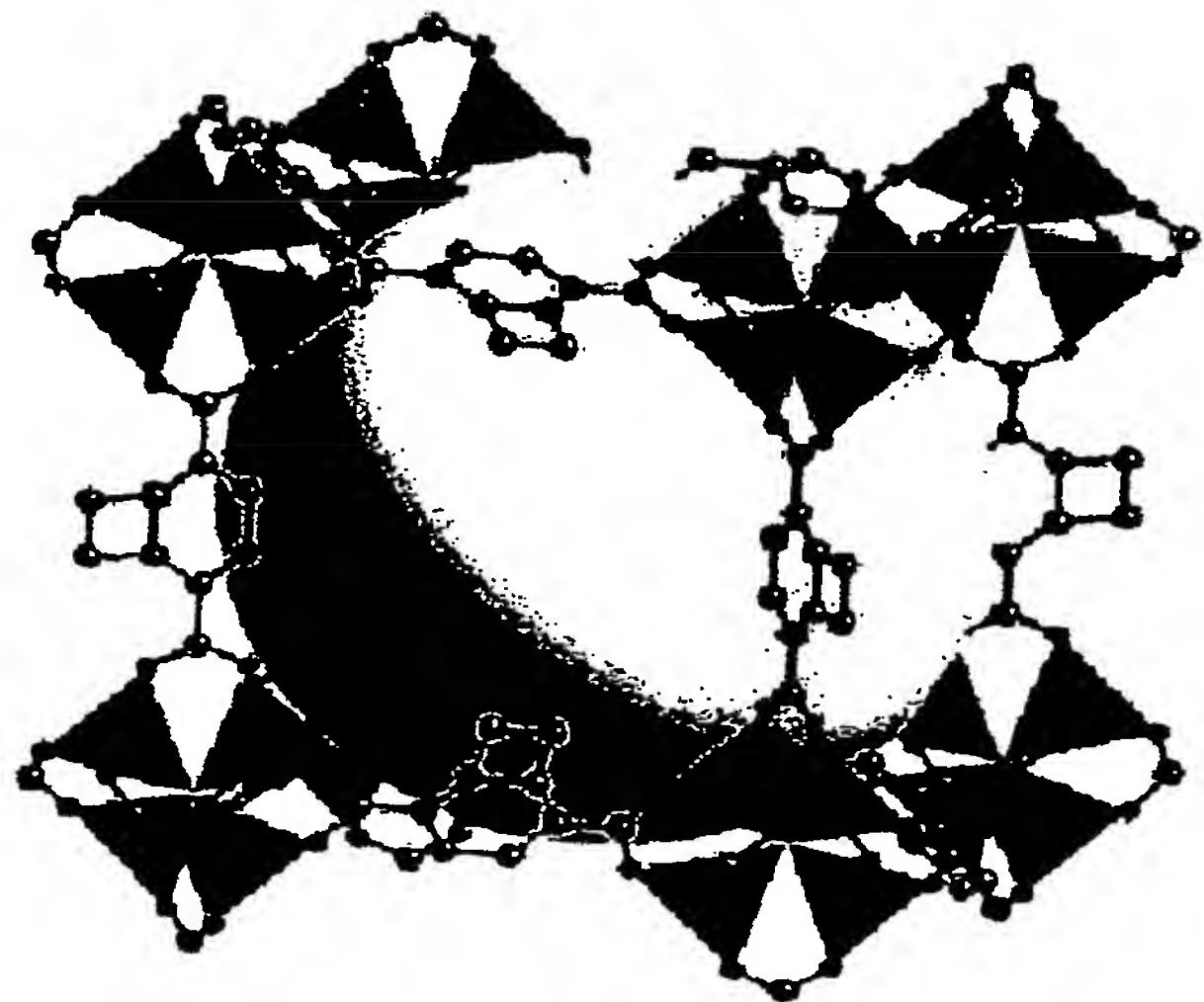
**Figure 40**



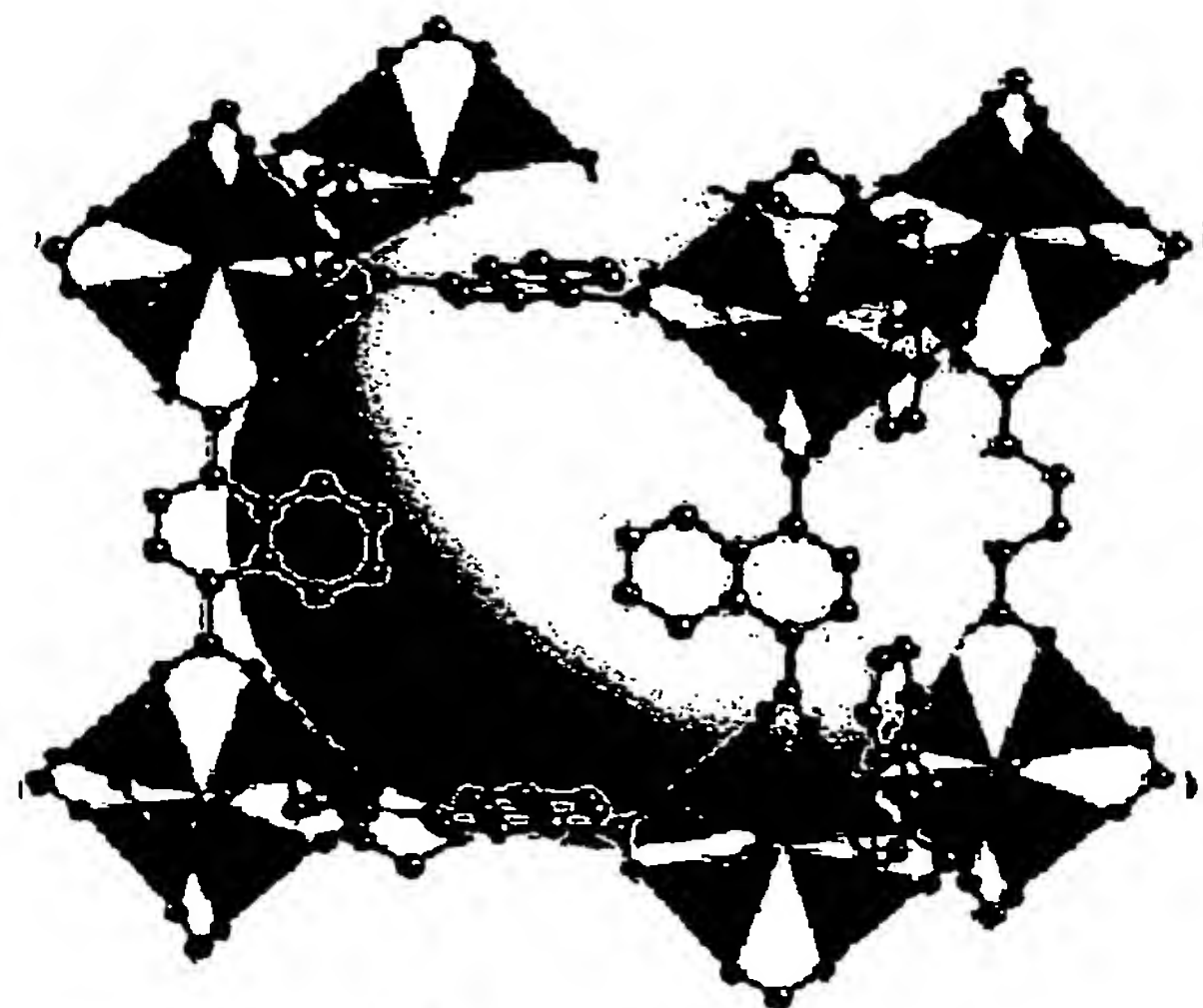
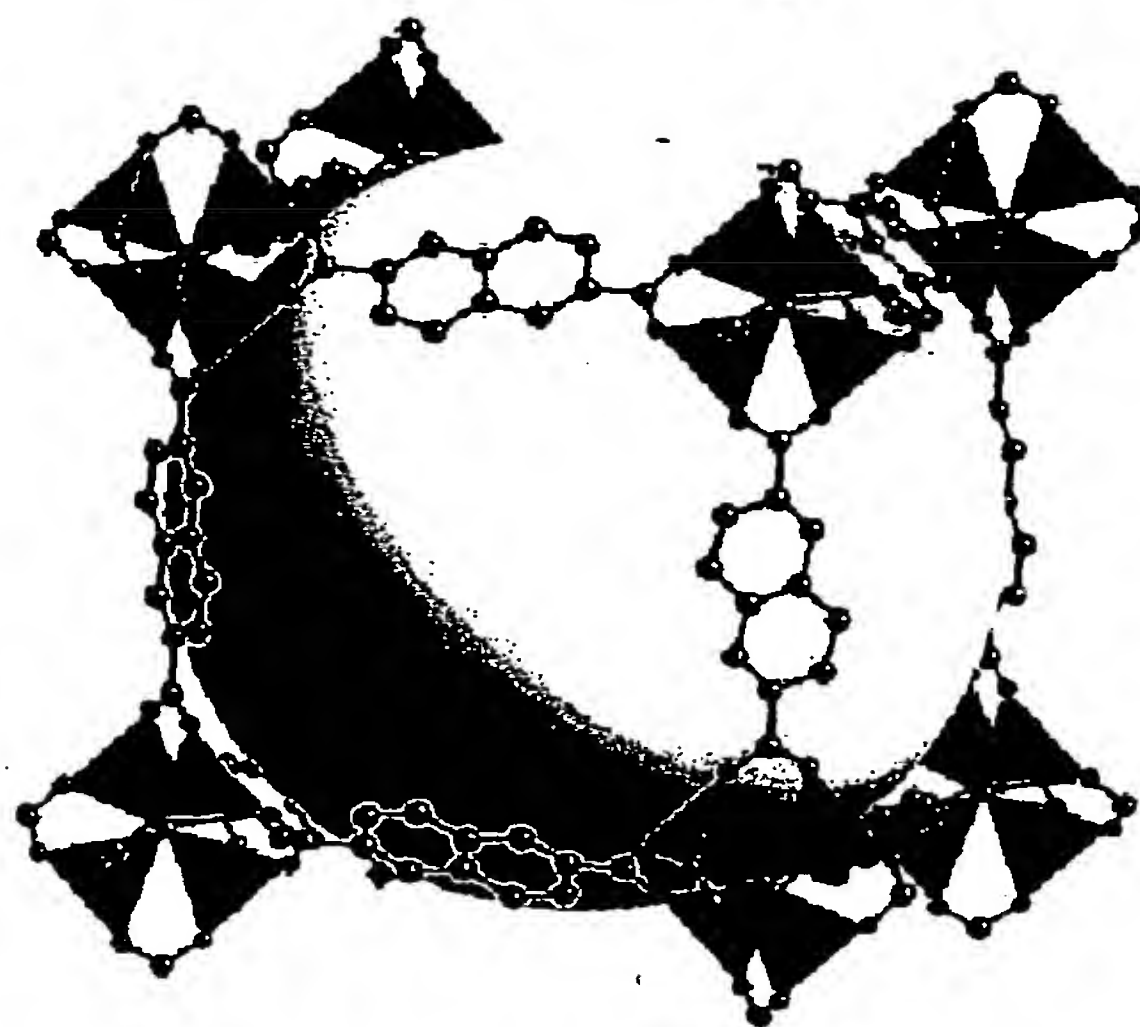
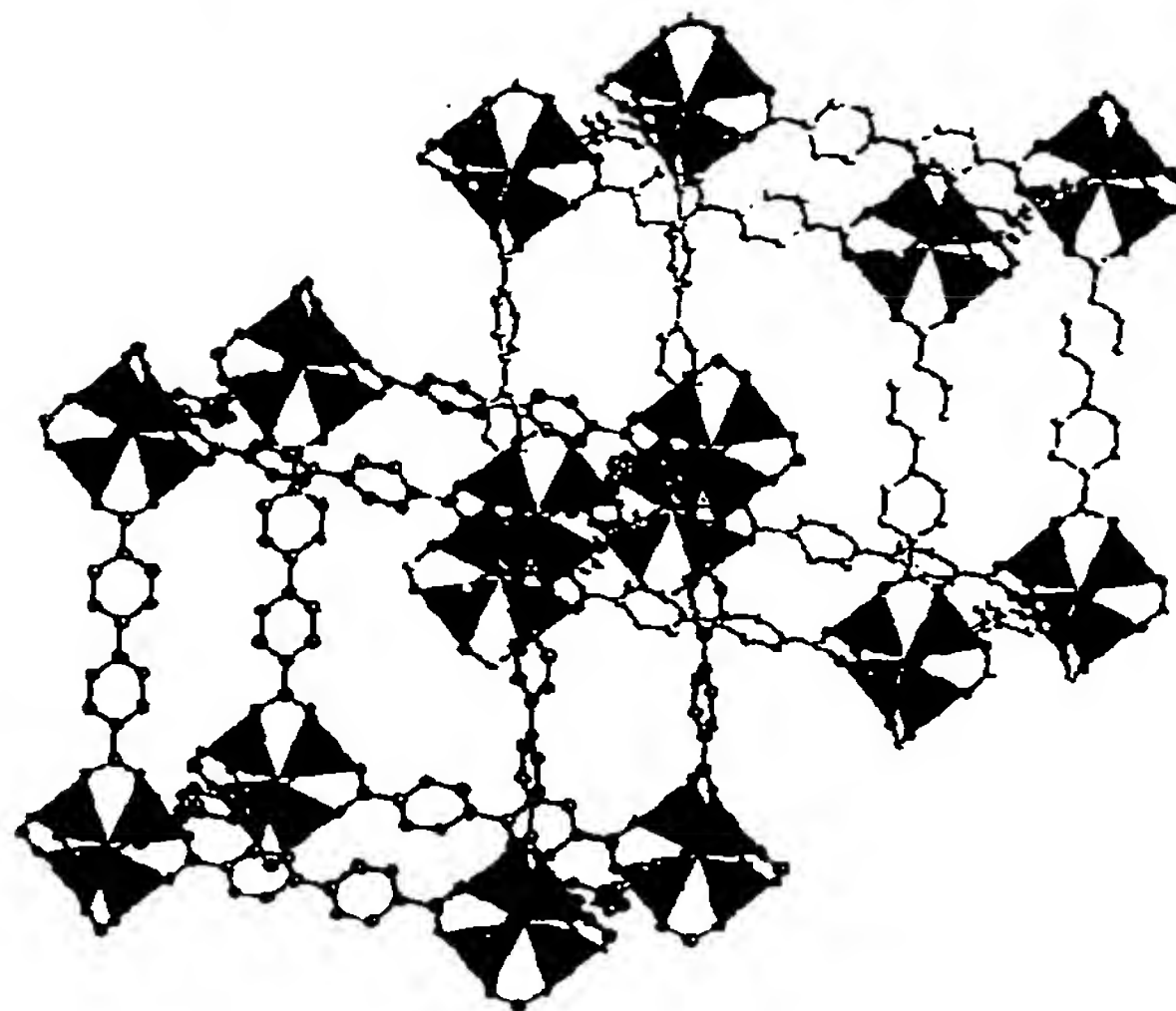
**Figure 41**



**Figure 42**

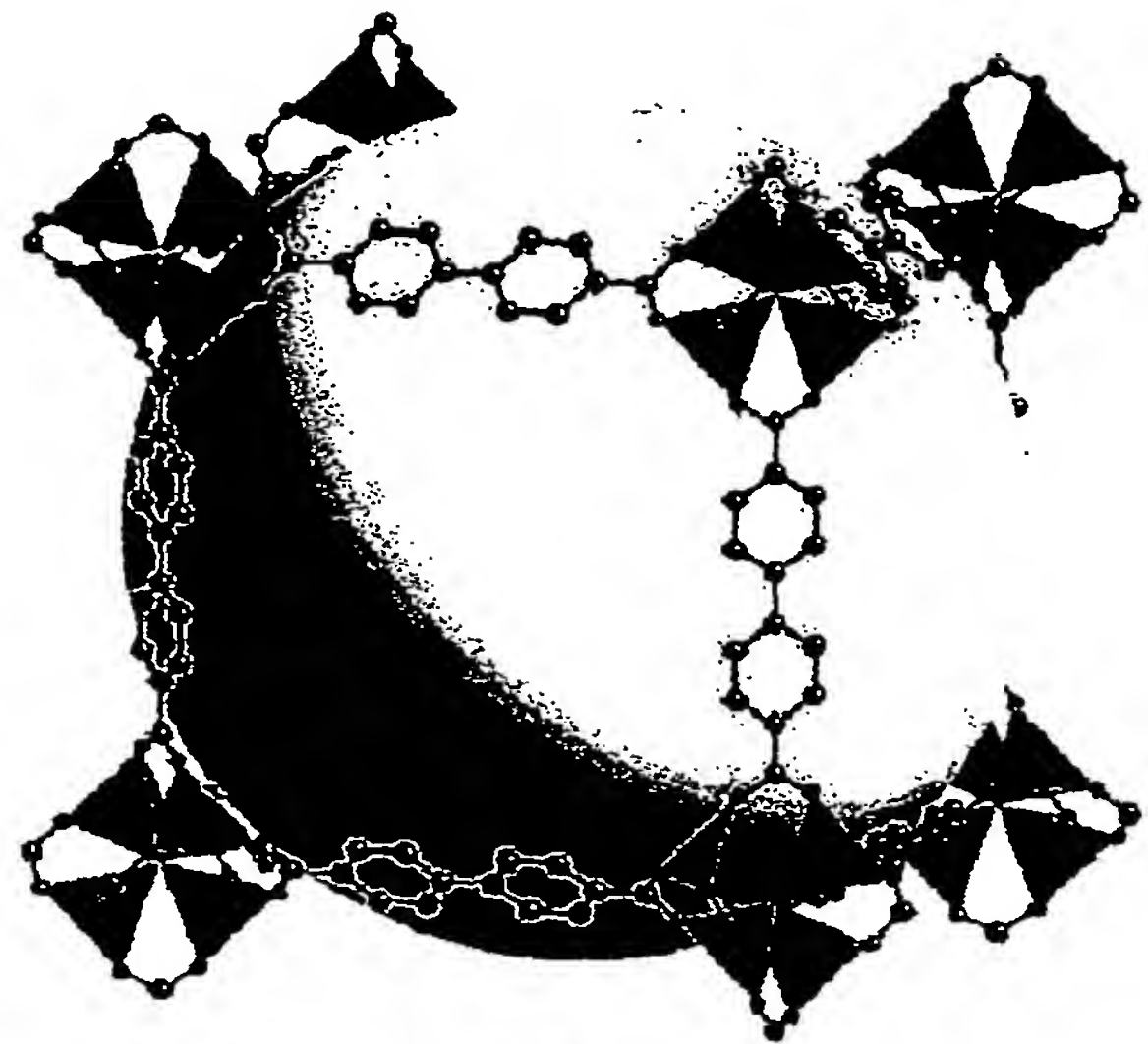


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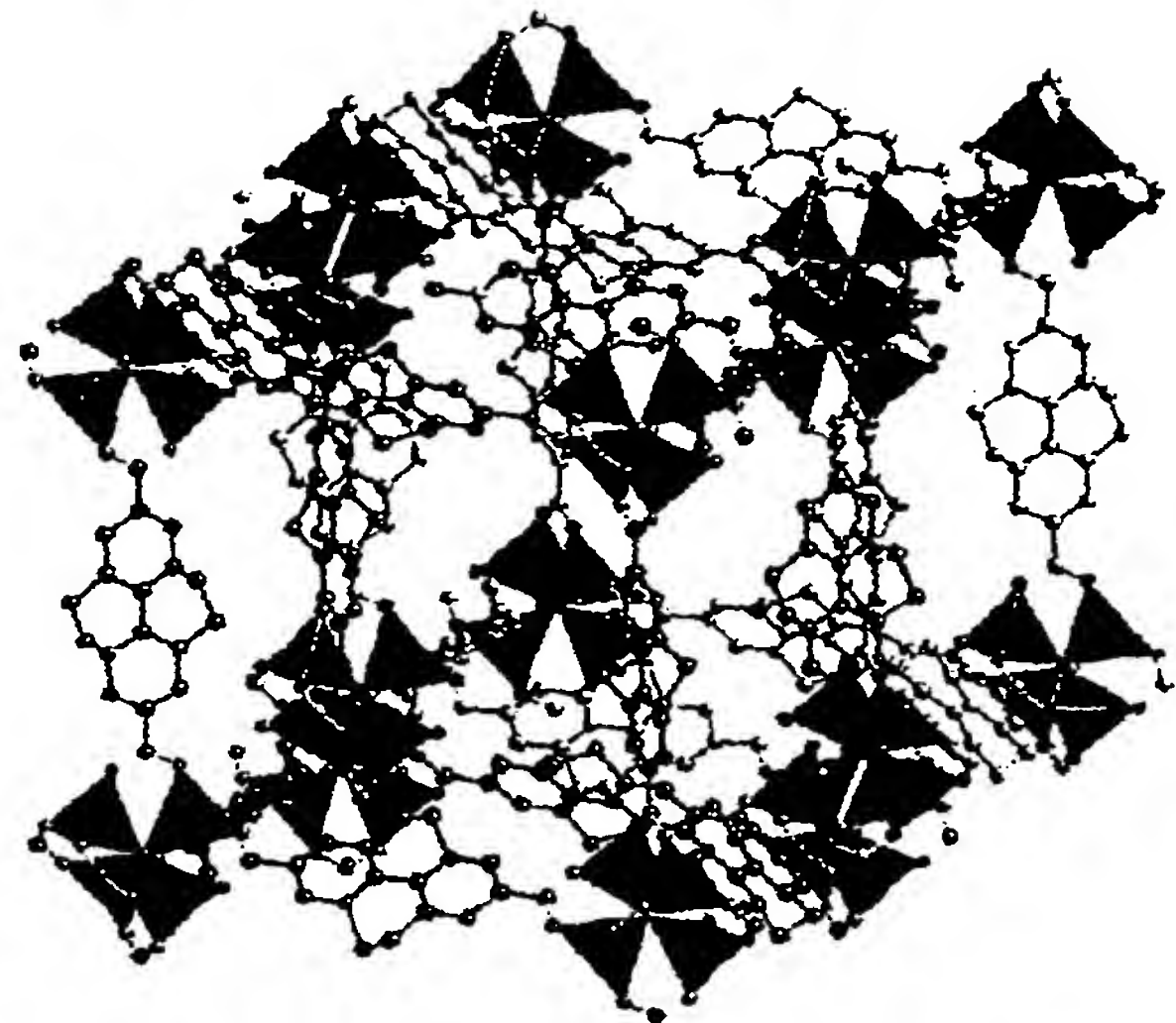
**Figure 43****Figure 44****Figure 45**

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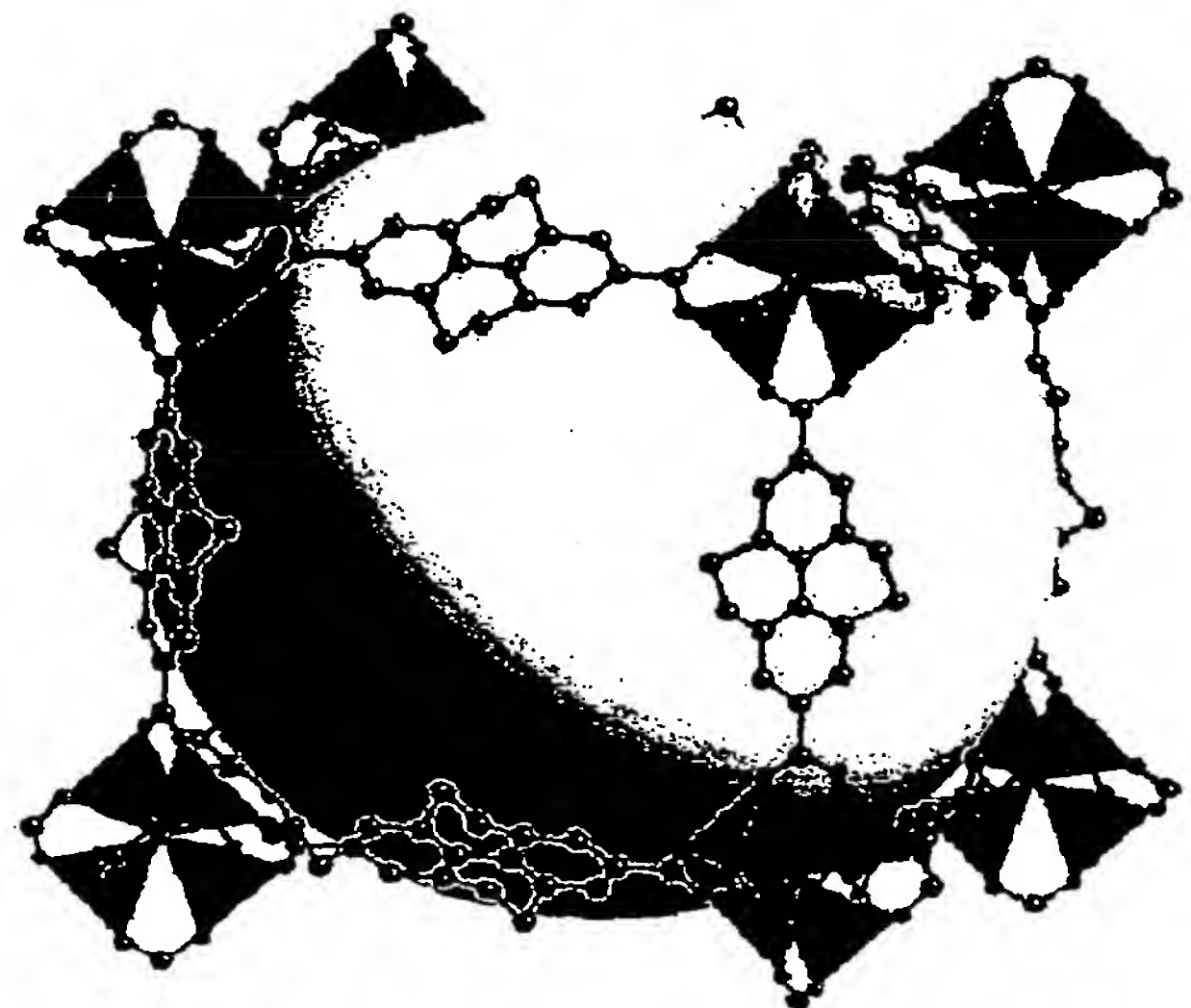
**Figure 46**



**Figure 47**

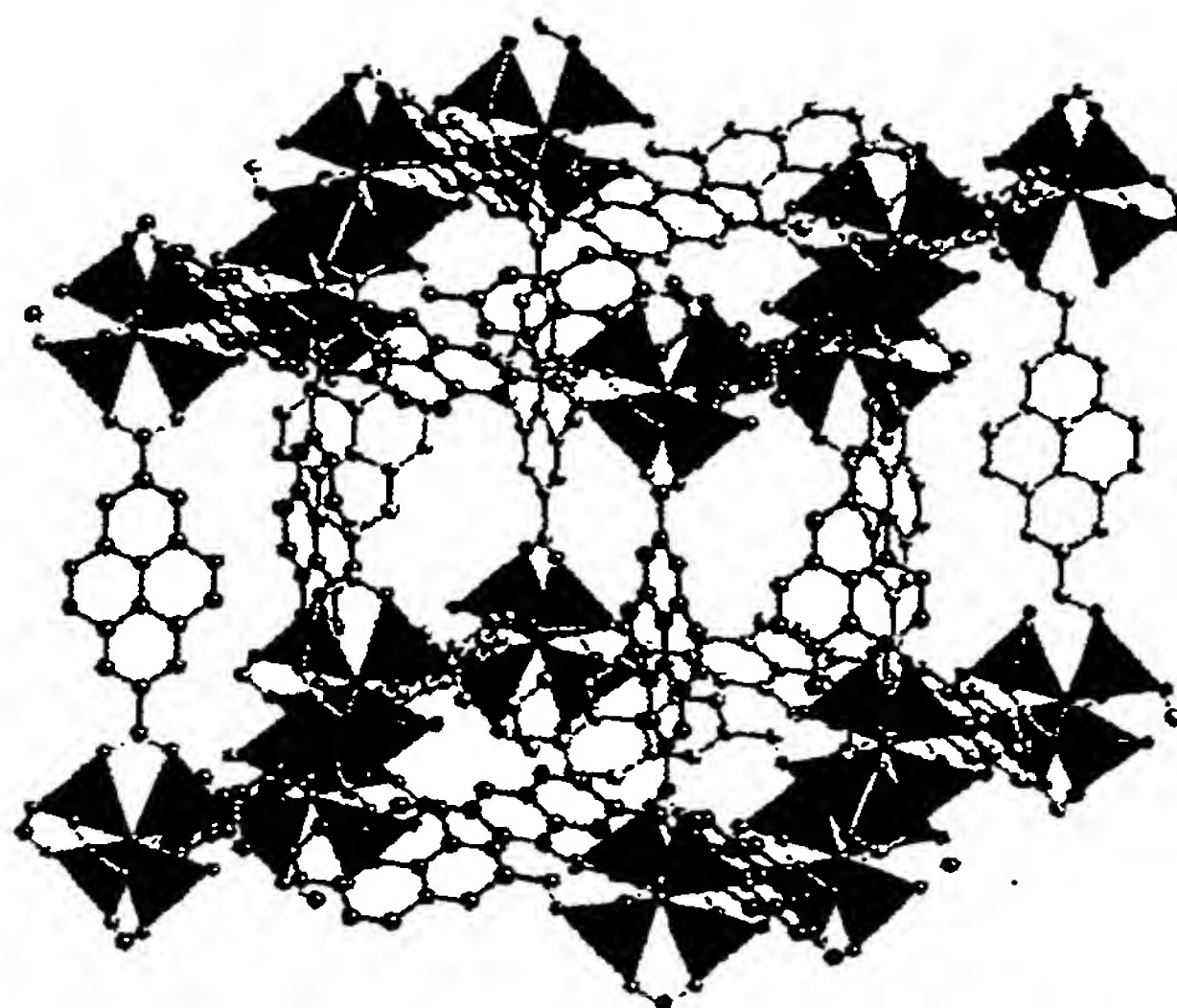
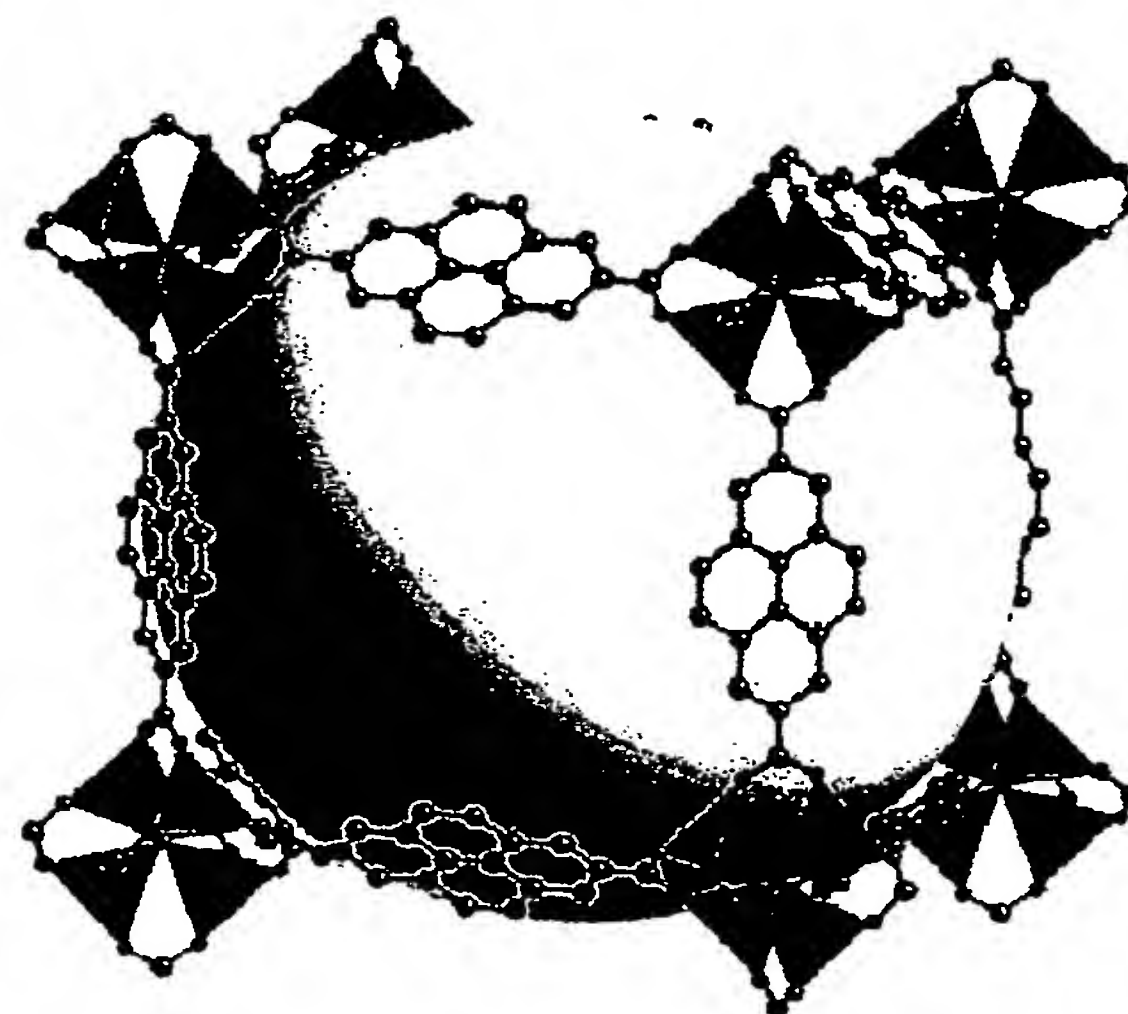
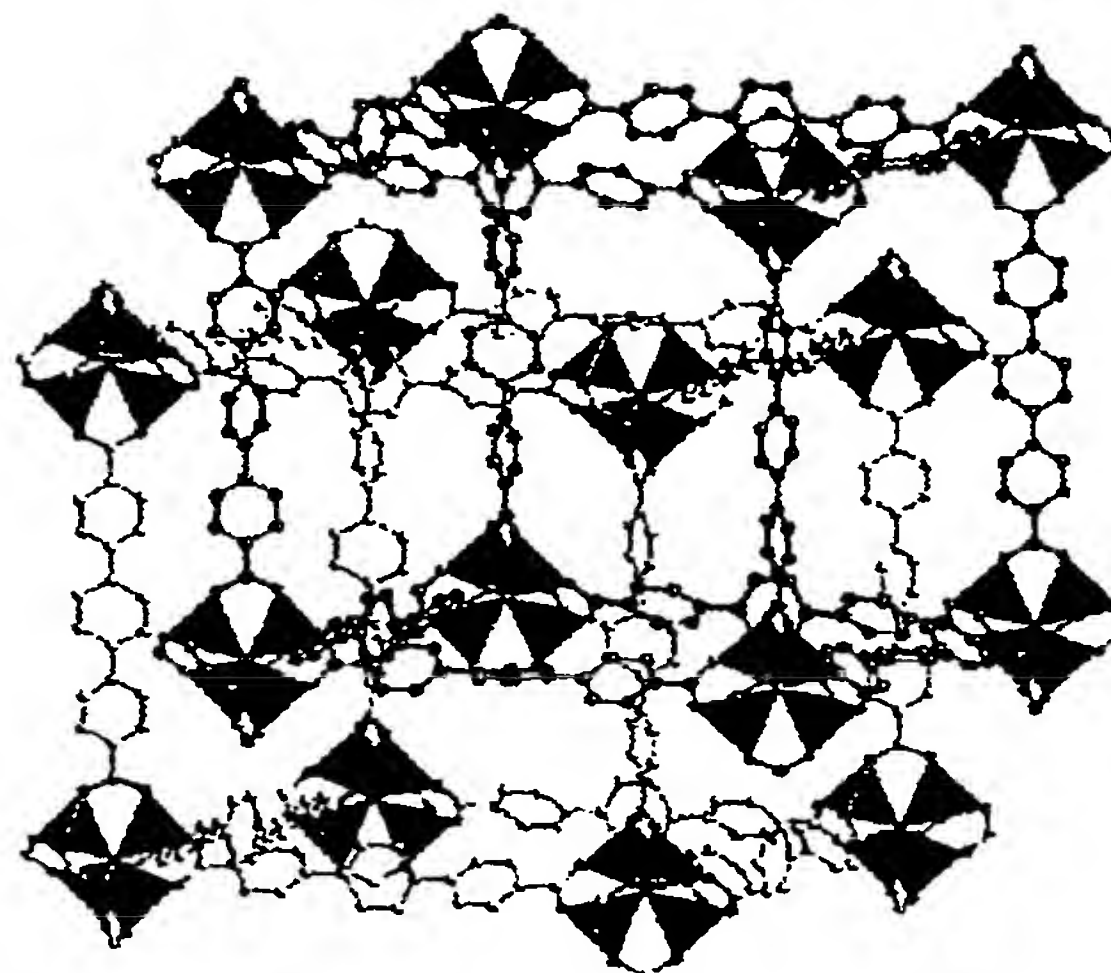


**Figure 48**



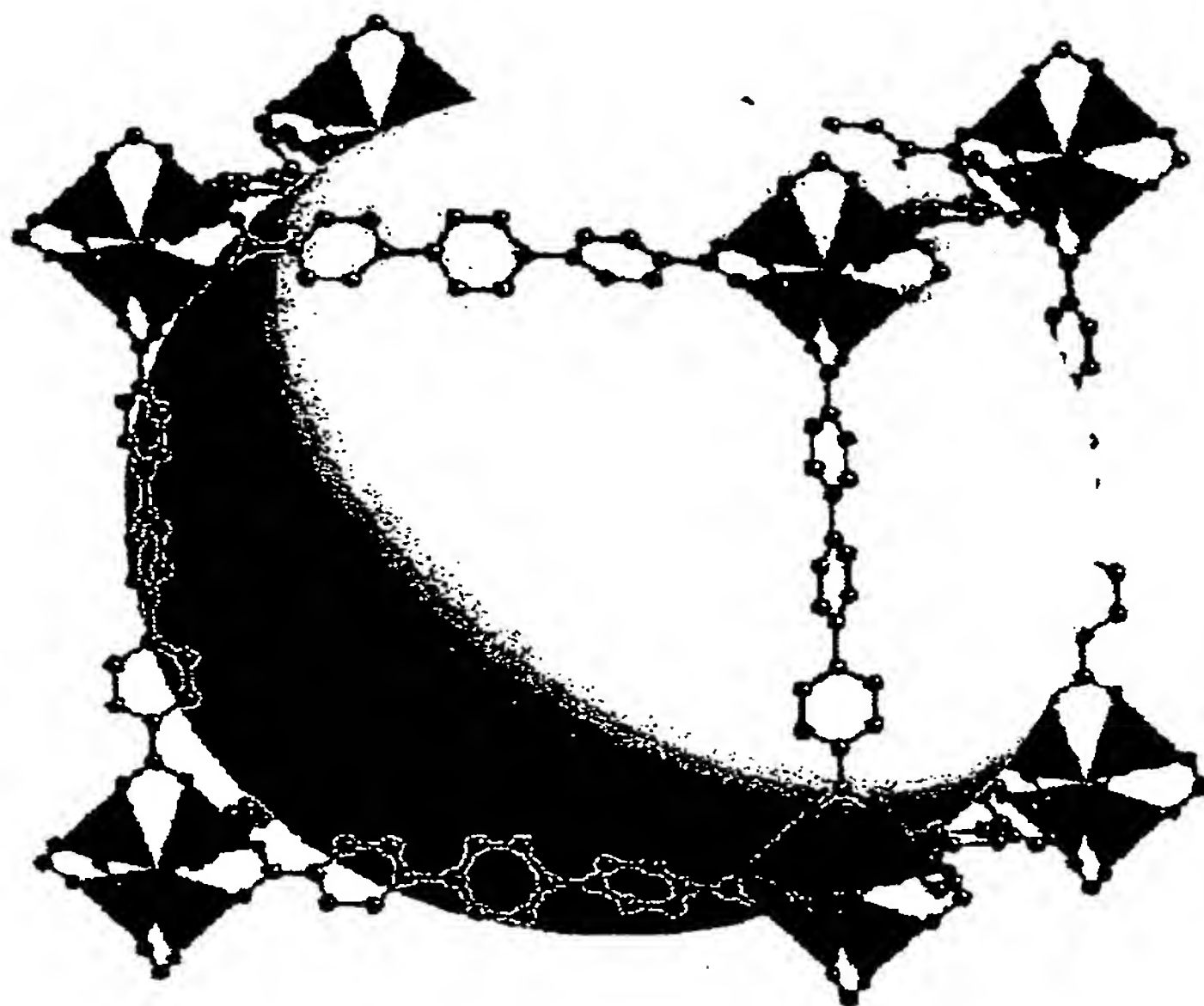


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**Figure 49****Figure 50****Figure 51**

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**Figure 52**



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Figure 53A

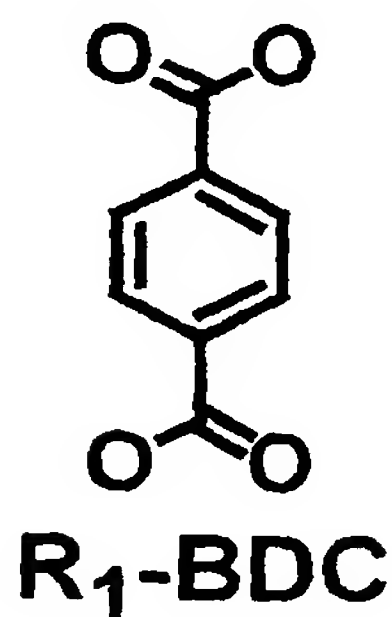


Figure 53B

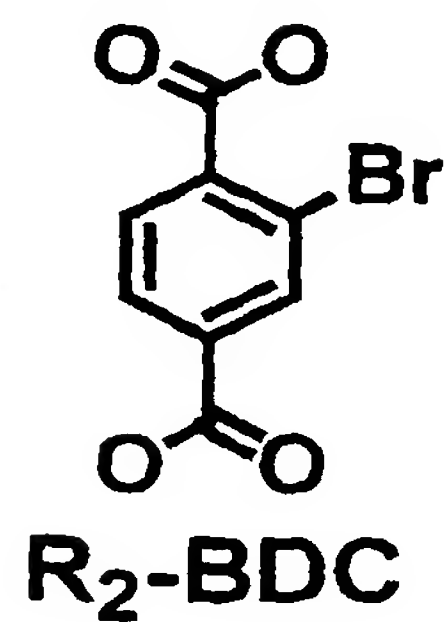


Figure 53C

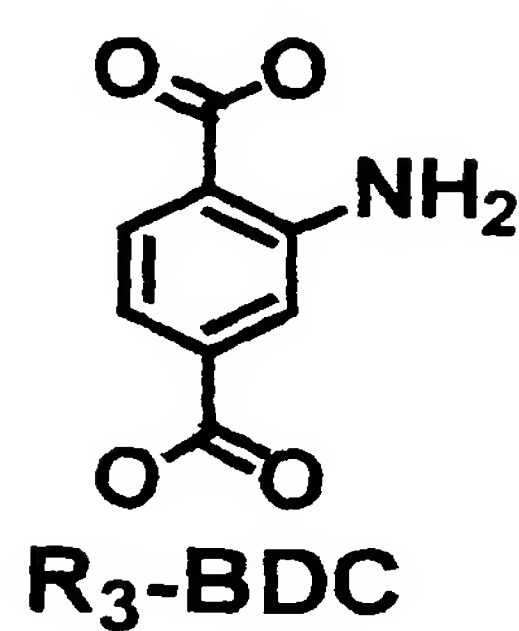


Figure 53D

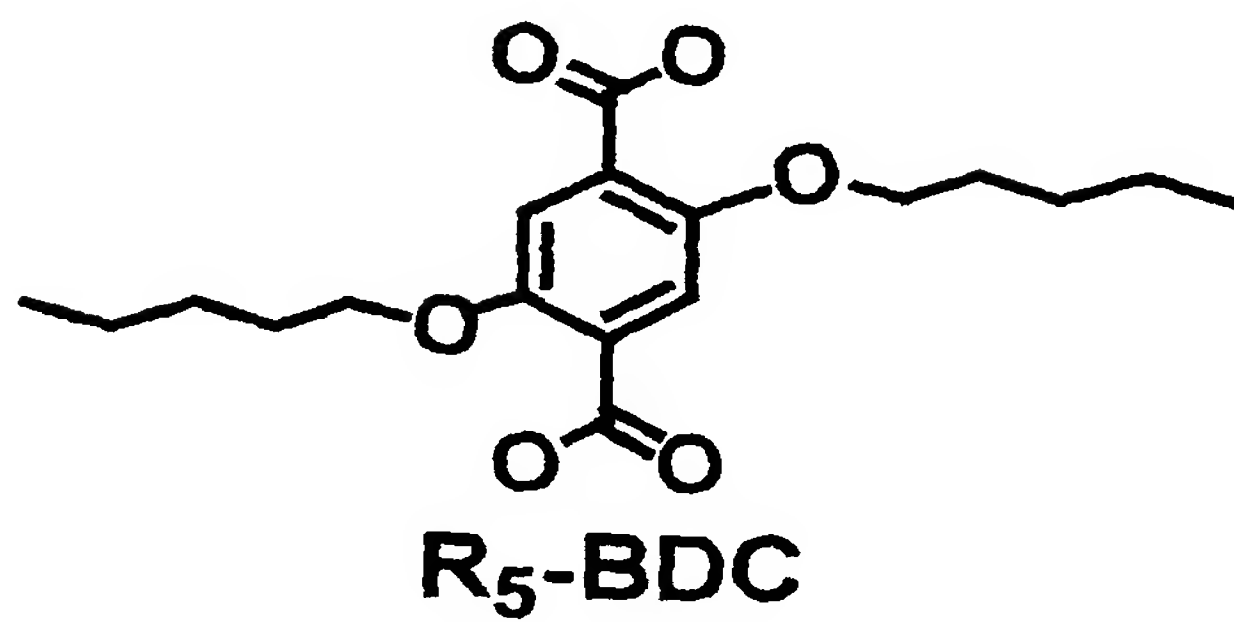
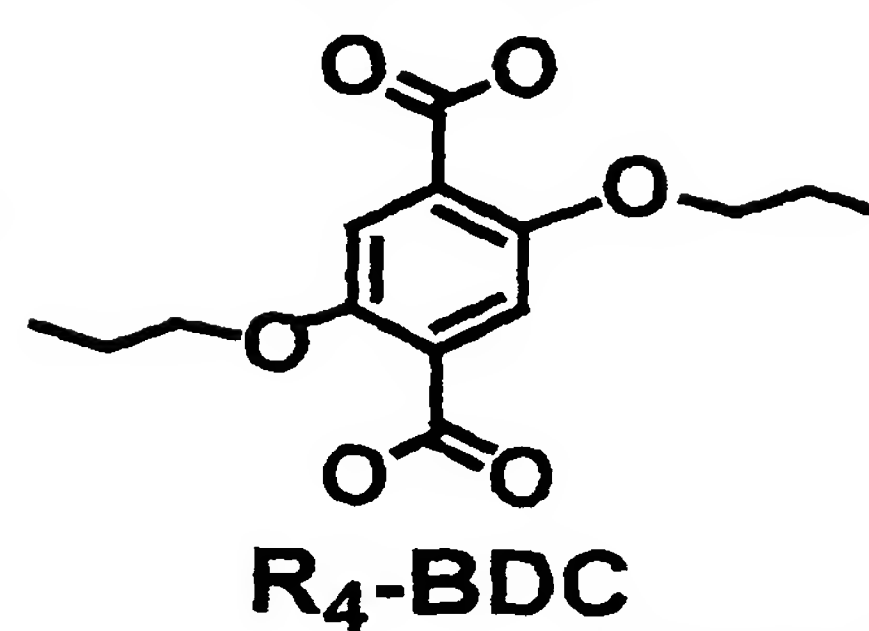


Figure 53E

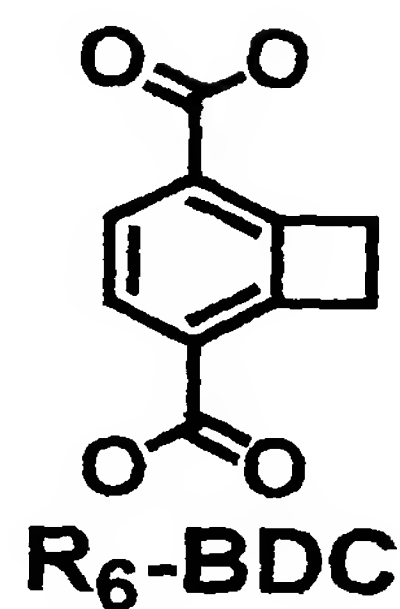


Figure 53F

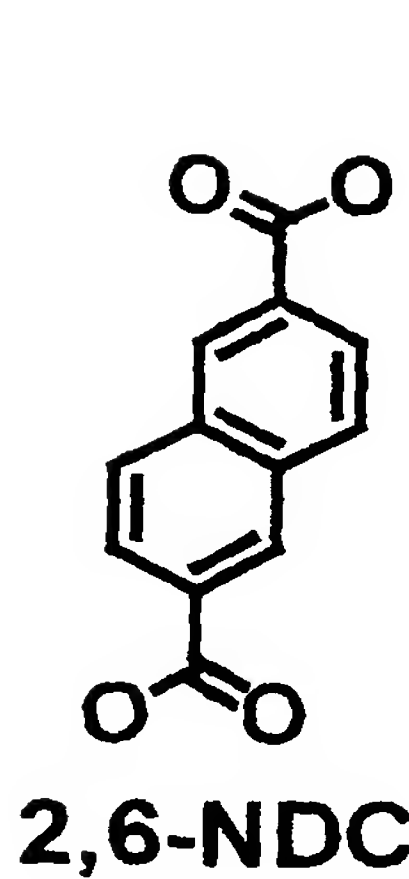
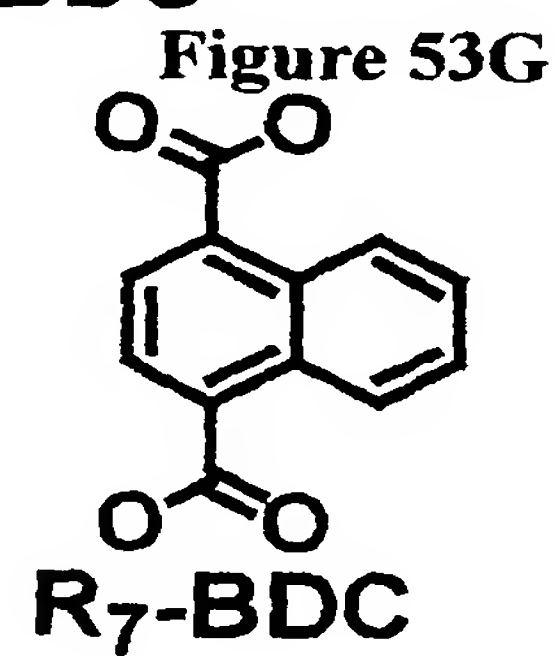


Figure 53H

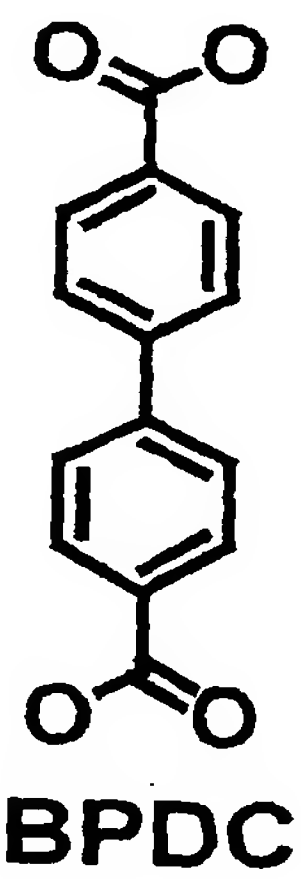


Figure 53I

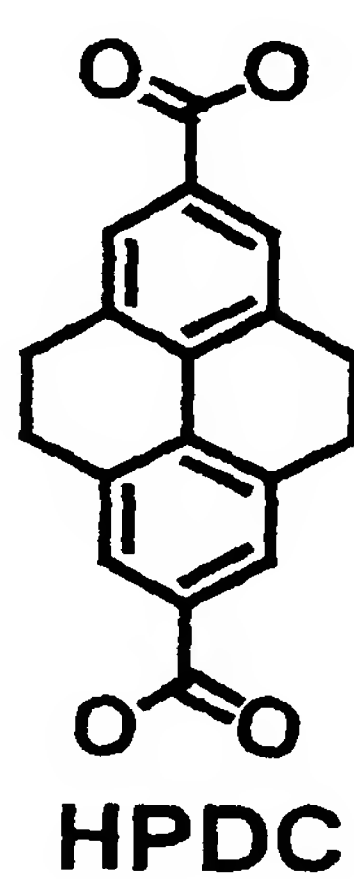


Figure 53J

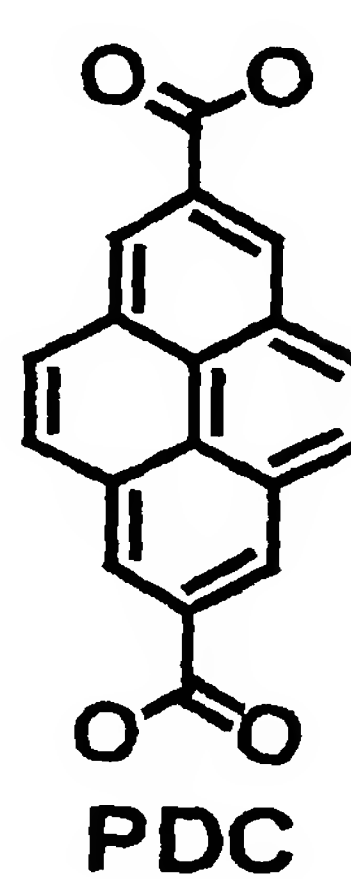


Figure 53K

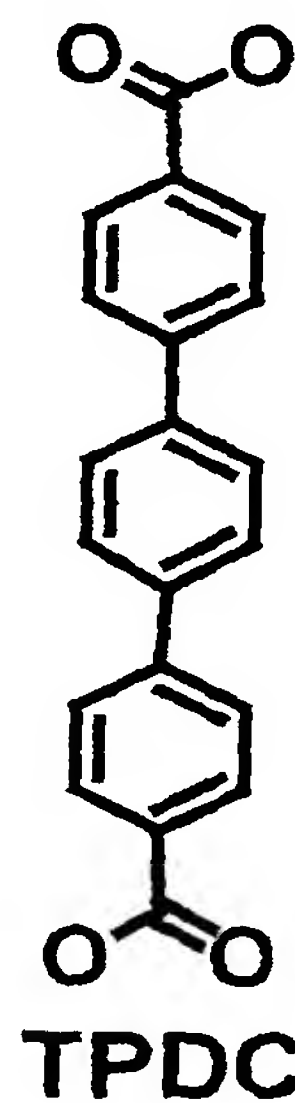


Figure 53L



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■ Fixed diameter □ Free diameter

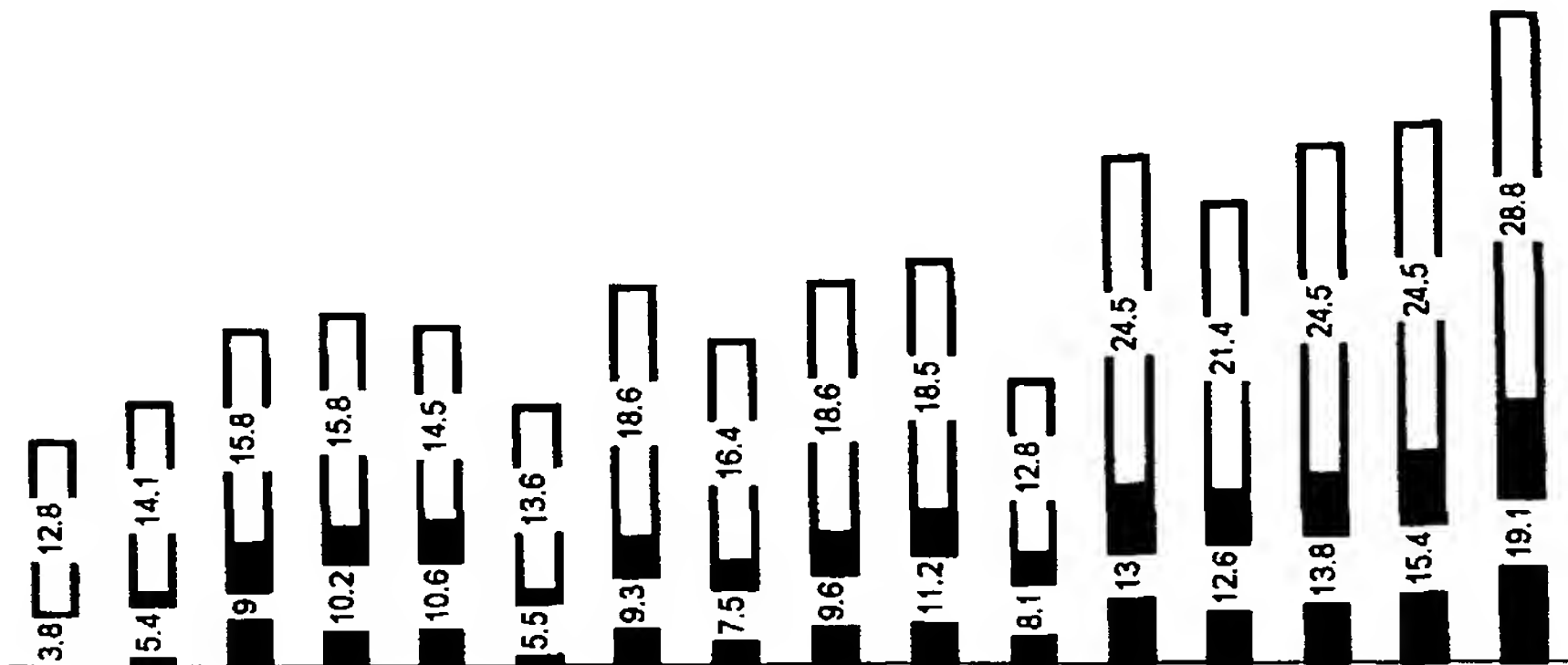


Figure 54C

■ Crystal density

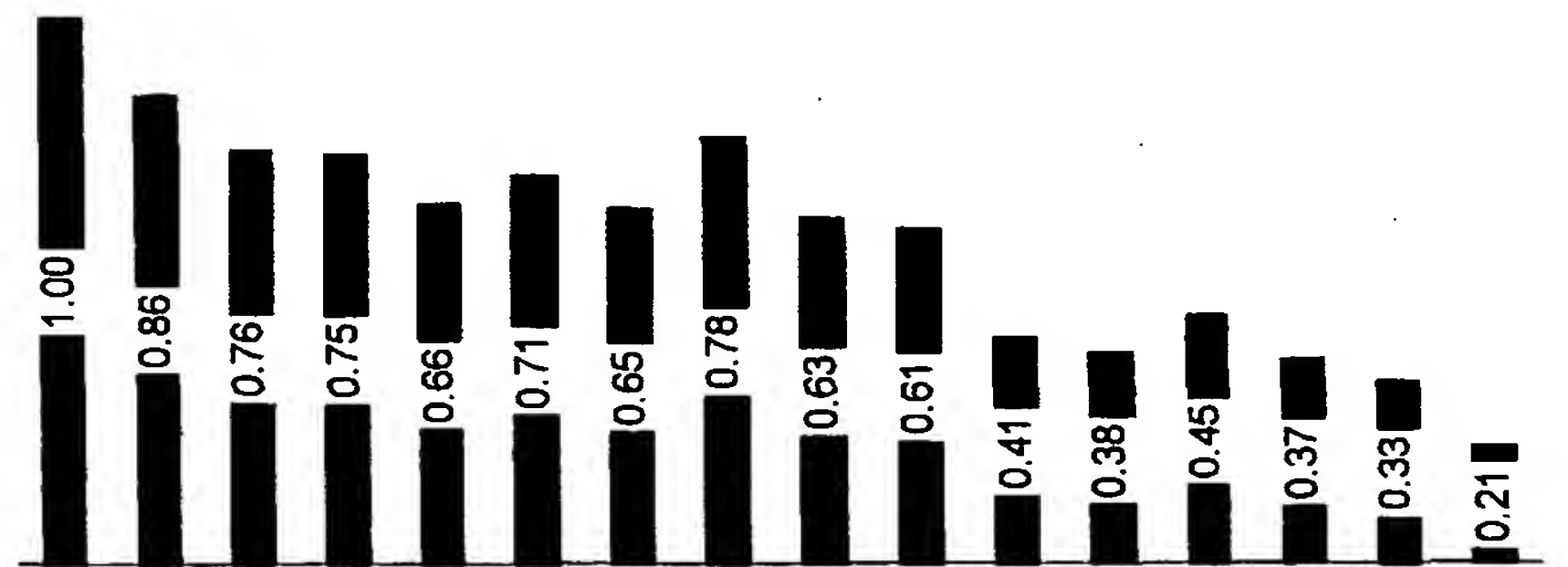


Figure 54B

■ % Free Volume

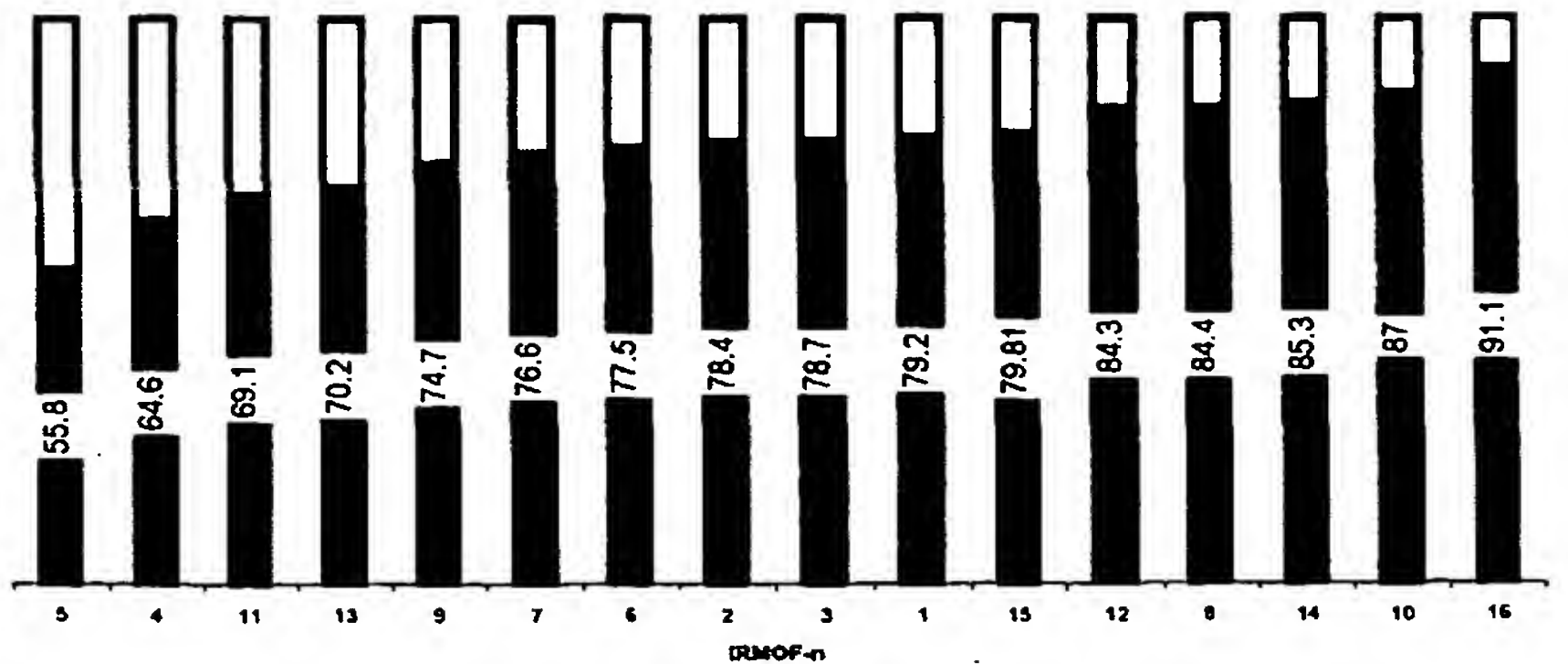


Figure 54A

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Figure 55A

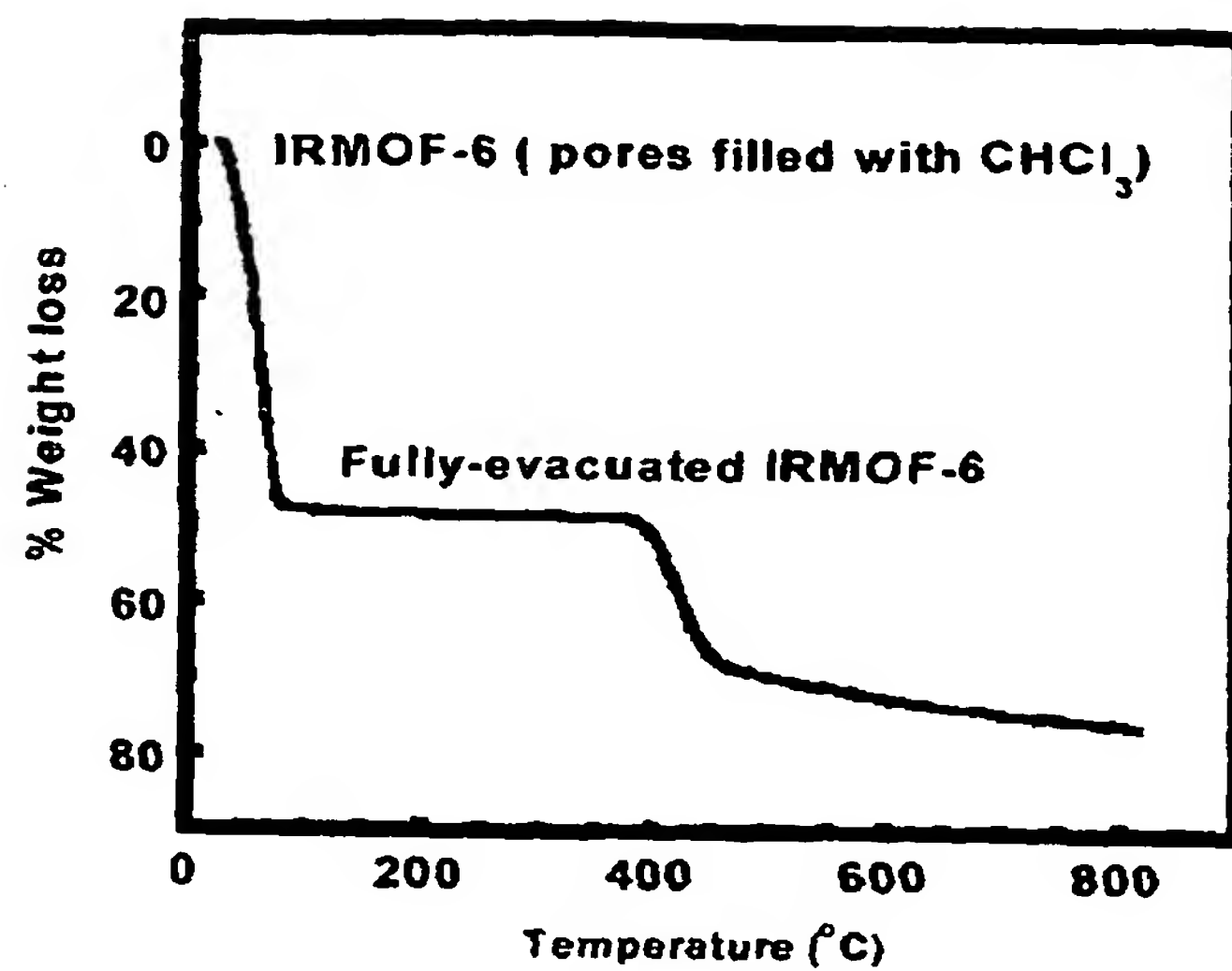


Figure 55B

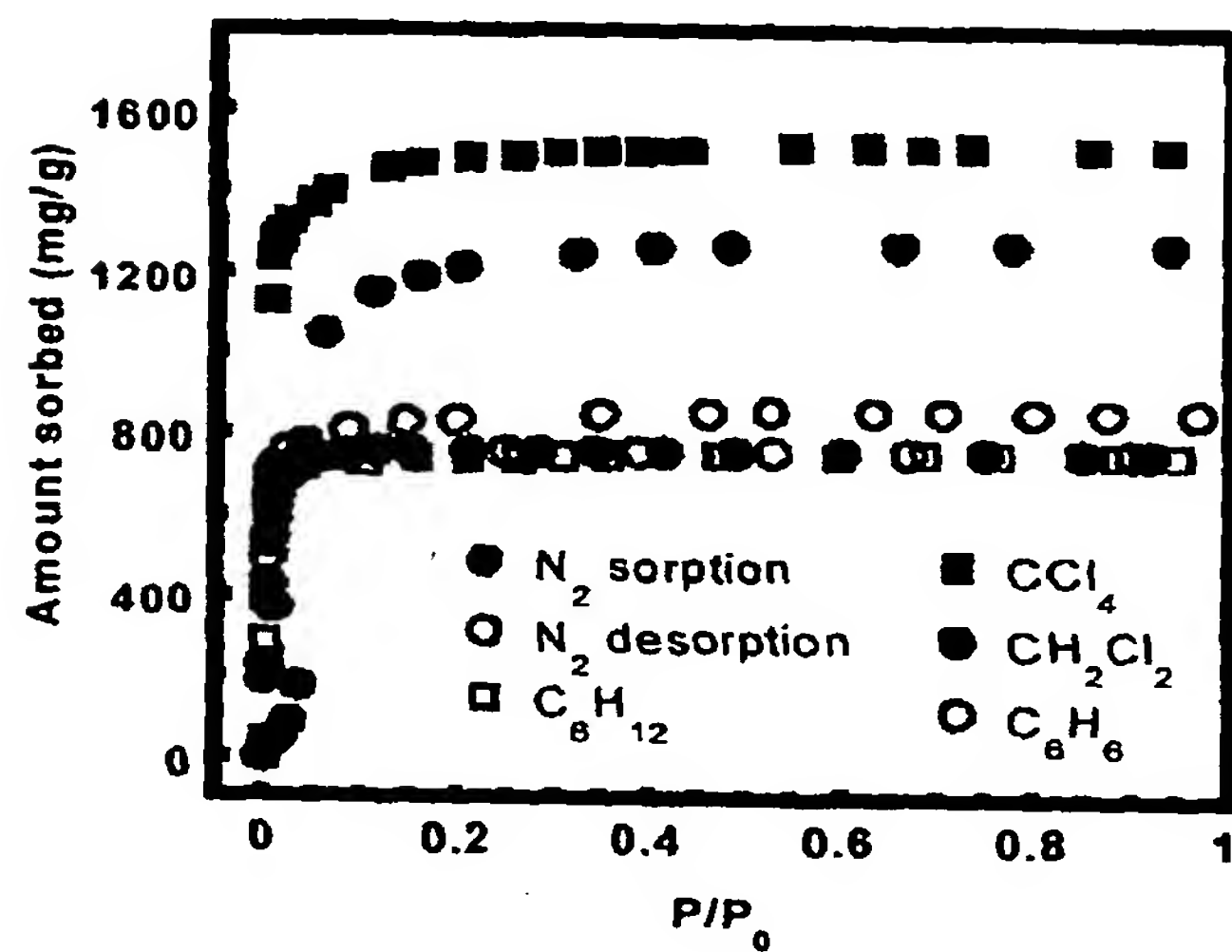
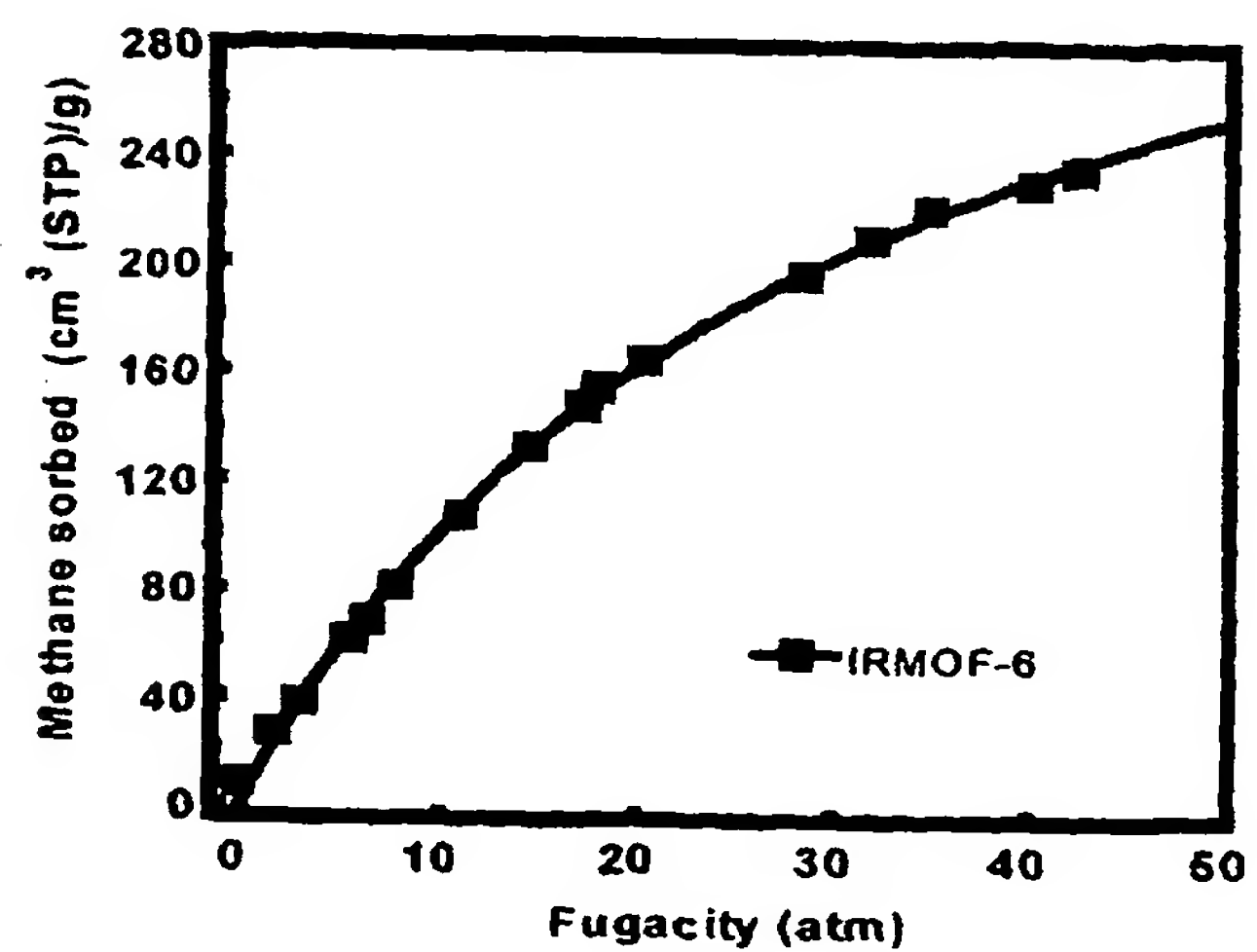
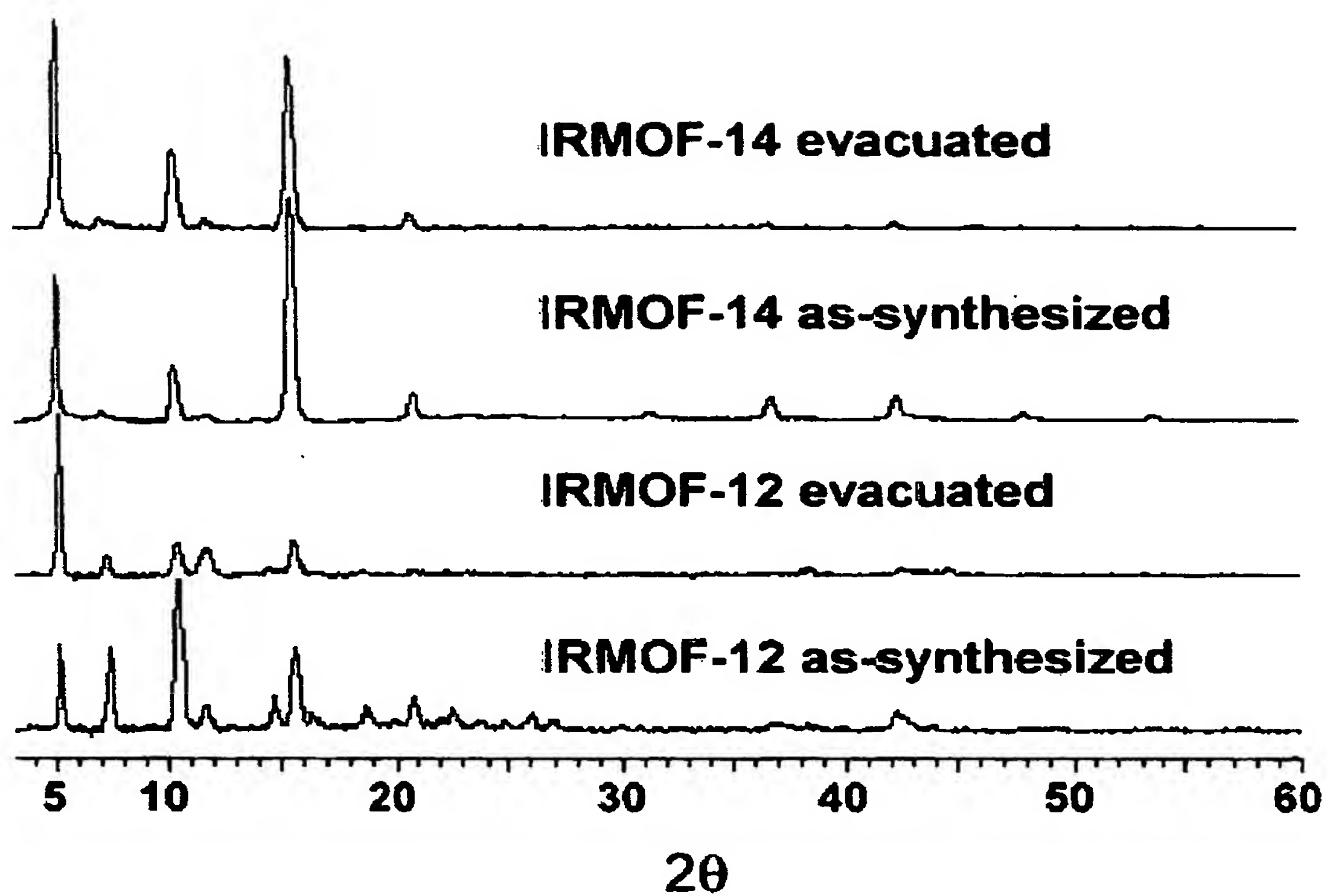


Figure 55C



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**Figure 55D**

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/13763

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C07F3/00 F17C11/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F F17C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LI, HAILIAN ET AL: "Design and synthesis of an exceptionally stable and highly porous metal-organic framework" NATURE (LONDON) (1999), 402(6759), 276-279  ' XP002210427 cited in the application the whole document  ---	1,4-11, 13
A	US 5 648 508 A (YAGHI OMAR M) 15 July 1997 (1997-07-15) cited in the application the whole document  ---	1,5,11
A	WO 99 05151 A (KEPERT CAMERON JOHN ;ROSSEINSKY MATTHEW JONATHAN (GB); ISIS INNOVA) 4 February 1999 (1999-02-04) the whole document  -----	1,5,11

☐ Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

21 August 2002

Date of mailing of the international search report

03/09/2002

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/13763

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5648508	A	15-07-1997	DE 69619093 D1	21-03-2002
			DE 790253 T1	19-02-1998
			EP 0790253 A2	20-08-1997
WO 9905151	A	04-02-1999	EP 1001960 A1	24-05-2000
			WO 9905151 A1	04-02-1999
			JP 2001510845 T	07-08-2001
			US 6372932 B1	16-04-2002

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